U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-261 070

A Mechanism for Ash Assisted Sludge Dewatering

Lehigh Univ, Bethlehem, Pa Center for Surface and Coatings Res.

Prepared for

Municipal Environmental Research Lab, Cincinnati, Ohio Wastewater Research Div

Dec 76

350144

PB 261 070

EPA-600/2-76-297
December 1976

A MECHANISM FOR ASH ASSISTED SLUDGE DEWATERING

by

F. J. Micale
Sinclair Laboratory, Lehigh University
Bethlehem, Pennsylvania 18015

Grant No. 17030 ECM

Project Officer
J. E. Smith, Jr.
Wastewater Research Division
Municipal Environmental Research Laboratory
Cincinnati, Ohio 45268

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/2-76-297		

4. TITLE AND SUBTITLE	5. REPORT DATE
MECHANISM FOR ASH ASSISTED SLUDGE DEWATERING	December 1976 issuing date
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
F. J. Micale	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Center for Surface and Coatings Research Sinclair Laboratory, Lehigh University Bethlehem, Pennsylvania 18015	1BC611
	11. CONTRACT/GRANT NO.
	xxxxxxxx 17030 ECM
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Municipal Environmental Research Laboratory Office of Research and Development U. S. Environmental Protection Agency Cincinnati, Ohio 45268	Final; 6/1/69 - 8/31/71
	14. SPONSORING AGENCY CODE EPA-ORD

15. SUPPLEMENTARY NOTES

16. ABSTRACT The ability of various additives to improve the dewaterability of activated sludge was determined and the surface properties of additives characterized in order to arrive at a mechanism for ash conditioning of activated sludge. The primary additives investigated were fly ash and 3 sludge incinerator ashes. All 4 ashes had high surface areas, 1.7 to 17 m^2/g, a hydrophilic surface and a high concentration of water soluble salts. Since the presence of salts and a solid surface complicates the interpretation of experimental results, a series of experiments was devised where either salts or solids alone were added to the activated sludge for settleability measurements. The solids consisted of the washed ashes themselves, as well as two silicas, two carbon samples, and magnetite, which contained high surface areas and exhibited different surface properties. The salts consisted of the washings obtained from the ashes and a number of inorganic salts and ionic polymeric surfactants.

All 4 ashes greatly increased the rate of settling of activated sludge in the order Tahoe > Kansas > Millcreek > Beckjord. Repeated washing of the ashes had the effect of decreasing the rate of settling. A dual mechanism, which was based on coulombic interaction between sludge particles and solid additives, was proposed. This same mechanism explains why fly ash and sludge incinerator ash have been found by other investigators to be capable of increasing the productivity of both pressure filters and vacuum filters.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Ashes, Fly ash, Inorganic salts, Surface properties Sludge, Activated sludge, Treatment, Concentrating, Thickening, Dewatering	Sludge incinerator ash, Beckjord fly ash, Millcreek sludge incinerator ash, Lake Tahoe sludge incinerator ash	13B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	62
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (9-73)

DISCLAIMER

This report has been reviewed by the Municipal Environmental Research Laboratory, U. S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution, and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and is a most vital communications link between the researcher and the user community.

The research reported here was performed for the Ultimate Disposal Section of the Wastewater Research Division to determine the properties of a variety of ashes. These properties were then related to various researchers' findings on improved sludge settleability and dewaterability with ash addition. A prescription is suggested for the kind of ash that is required to improve a sludge's dewaterability.

F. T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

The ability of various additives to improve the dewaterability of activated sludge was determined and the surface properties of the additives were characterized to arrive at a mechanism for the ash conditioning of activated sludge. The primary additives investigated were fly ash and three sludge incinerator ashes. All four ashes had high surface areas (1.7 to 17 m^2/g), a hydrophilic surface, and a high concentration of water soluble salts. Since the presence of salts and a solid surface complicates the interpretation of experimental results, a series of experiments was devised where either salts or solids alone were added to the activated sludge for settleability measurements. The solids consisted of the washed ashes themselves as well as two silicas, two carbon samples, and magnetite, which contained high surface areas and exhibited different properties. The salts consisted of the washings obtained from the ashes and a number of inorganic salts and ionic polymeric surfactants.

All four ashes greatly increased the rate of settling of activated sludge in the order Tahoe > Kansas > Millcreek > Beckjord. Repeated washing of the ashes had the effect of decreasing the rate of settling and changed the relative efficiency to Kansas > Millcreek > Beckjord > Tahoe. The hydrophilic silica carbon black and magnetite greatly increased the rate of settling, while hydrophobic silica and graphon had very little effect. Halide salts and only the cationic polymeric surfactant were capable of increasing the rate settling. A dual mechanism, which was based on coulombic interaction between sludge particles and solid additives, was proposed. This same mechanism explains why fly ash and sludge incinerator ash have been found by other investigators to be capable of increasing the productivity of both pressure filters and vacuum filters.

CONTENTS

Foreword		iii
Abstract		iv
Tables		v
Figures		vi
Acknowledgements		ix
Section		
I	Introduction	1
II	Conclusions	5
III	Recommendations	7
IV	Experimental	9
V	Characterization of Solid Additives	11
VI	Discussion of Results	49
VII	References	53

LIST OF TABLES

Number		Page
1	BET Surface Areas of Ash Samples	14
2	Surfactant Solution Adsorption and Electrophoretic Mobility of Ash Samples	33

LIST OF FIGURES

Number		Page
1	Particle size distribution of Millcreek and Lake Tahoe incinerator ashes	12
2	Particle size distribution of Beckjord fly ash and Kansas incinerator ash	13
3	X-Ray diffraction pattern of incinerator ashes and reference standards	15
4	X-Ray diffraction pattern of Beckjord fly ash and reference standards	16
5	Conductivity and pH of ash dispersion as a function of particle size	17
6	pH of ash dispersion as a function of number of washings	19
7	Conductivity of ash dispersions as a function of number of washings	20
8	Conductivity and pH of total ash dispersions as a function of time	21
9	pH of total ash dispersions as a function of concentration in deionized water and activated sludge	22
10	Water adsorption isotherms on silica and carbon surfaces	23
11	Water adsorption isotherms on total ash samples	25
12	Isopropyl alcohol adsorption isotherms on silica and carbon surfaces	26
13	Isopropyl alcohol adsorption isotherms on total ash samples	28
14	Solution adsorption of DTAB onto carbon surfaces	29
15	Solution adsorption of DTAB onto silica surfaces	30
16	Solution adsorption of DTAB onto ash samples in units of millimole per gram	31

Number		Page
17	Solution adsorption of DTAB onto ash samples in units of molecules per 100 $\AA^2$	32
18	Settleability of activated sludge for 50 mg of ash additives	35
19	Reproducibility in settleability efficiency of Tahoe and Millcreek additives	35
20	Reproducibility in settleability efficiency of Beckjord and Kansas additives	37
21	Reproducibility in settleability efficiency of Tahoe ash over a 12 month period	37
22	Settleability of activated sludge as a function of concentration of Lake Tahoe additive	38
23	Settleability of activated sludge as a function of concentration of Kansas additive	38
24	Settleability of activated sludge as a function of concentration of Millcreek additive	39
25	Settleability of activated sludge as a function of concentration of Beckjord additive	39
26	Comparison of washed ash, unwashed ash, and ash washings for Lake Tahoe additives on settleability	40
27	Comparison of unwashed (total) ash, washed ash and ash washings for Kansas additives on settleability	40
28	Comparison of unwashed ash, washed ash and ash washings for Millcreek additive on settleability	41
29	Comparison of unwashed ash, washed ash and ash washings for Beckjord additive on settleability	41
30	Effect of different particle size fraction of 50 mg of Beckjord additive on settleability	43
31	Effect of different particle size fraction of 10 mg of Beckjord additive on settleability	43
32	Comparison between the rate of settleability for 50 mg carbon and silica additives	44
33	Settleability of activated sludge as a function of concentration for two silicas additives	44
34	Settleability of activated sludge as a function of concentration of carbon additives	46

Number		Page
35	Settleability of activated sludge as a function of concentration of magnetite additive	46
36	Settleability of activated sludge as a function of concentration of calcium fluoride additive	47
37	Settleability of activated sludge as a function of concentration of aluminum chloride and potassium phosphate additive	47
38	Settleability of activated sludge for different Atlas polymeric flocculants (10 mg sample)	48
39	Settleability of activated sludge for a Nalco anionic polymeric flocculant	48

ACKNOWLEDGEMENTS

The planning, experimental work, and report preparation was performed by a team from Lehigh University consisting of Dr. A. C. Zettlemoyer, Dr. F. J. Micale, Dr. B. H. Bijsterbosch, Dr. D. Fairhurst, Mr. T. H. Chiu and Mr. R. Jacoby.

Mr. Dianniano, superintendent of Buildings and Grounds, Allentown College of St. Francis De Sales, Lower Saucon Township, Pennsylvania, is acknowledged for aid in obtaining activated sludge samples.

The support of this project by the U.S. Environmental Protection Agency's Office of Research and Development, and the help provided by Dr. R. B. Dean and Dr. J. E. Smith, Jr., the Grant Project Officers with the EPA's Municipal Environmental Research Laboratory, is acknowledged with sincere thanks.

SECTION I

INTRODUCTION

The continued quest for developing better methods of dewatering sewage sludge has led many investigators to investigate the properties of different additives such as lime and polymeric conditioning agents for facilitating dewatering. The high cost of these chemicals, along with the availability of inexpensive sources of fly ash and incinerator ashes, has more recently shifted the approach to utilizing ash solids as additives for the conditioning of sewage sludge. Vater, in his review of European practices in sludge dewatering and disposal [1], has reported effective use of both incinerator and fly as additives which increased vacuum filter yields. The levels of addition ranged from one to five parts of ash per part of sludge solid.

Work in the U. S. has been largely limited to laboratory scale experiments, with the Buchner Funnel test, using fly ash from coal combustion [2] [3]. Tenney [4], in a rather extensive investigation, has shown that the addition of fly ash to an activated sludge yields the following results: 1) the filtration time initially decreases rapidly with increasing fly ash concentration, followed by an increase in the filtration time with further addition of fly ash where the optimum level of fly ash addition was independent of percent of sludge solids in the range of 0.4 to 1%; 2) the filter cake thickness was directly proportional to the fly ash concentration from 0 to 200 mg fly ash per liter of sludge; 3) the percent of moisture in the filter cake decreased from 85% to a constant value of 60% with the addition of 50 mg of fly ash per liter of sludge; 4) the phosphate and COD content of the filtrate was decreased to a constant value with a fly ash concentration of 50 mg/l. Smith [5] has investigated the effects of adding both incinerator ash and fly ash to sewage sludge with respect to filter yield, cake moisture content and filtrate quality. The results of this investigation were: 1) the filter yield was proportional to ash dosage in the concentration range of 1.3 to 3.7 parts of ash per part of sludge solids for waste activated, raw primary or digested primary sludge, respectively; 2) the fly ash did not work as well as the incinerator ashes; 3) the moisture content of ash-conditioned sludge (ash-free basis) generally increased slightly for all sludges; and 4) the addition of ash produced a much clearer filtrate, which was lower in suspended solids but higher in dissolved solids.

Although previous workers have demonstrated that the addition of either incinerator ash or fly ash to sewage sludge has a definite affect on the filtering characteristics of these systems, a meaningful mechanism has not been proposed which is capable

of describing the experimental results. The reasons for this deficiency may be attributed to the complicated nature of both the sewage sludges and the ashes themselves, which consist of water soluble salts and a composite heterogeneous surface [4] [5]. Interpretation of filtering experiments, furthermore, are not straight forward in that the results are controlled by a delicate balance between particle-particle and particle-filter media interactions.

The approach adopted in this research program was to determine the effect which additives have on the sedimentation rate of activated sludges, where the sedimentation rate is proportional to the degree of flocculation of suspended solids, and to propose a mechanism whereby these additives affect the sludge particle/liquid interfacial properties so as to induce flocculation and improve dewatering. The primary additives investigated were incinerator ashes, which were obtained from Lake Tahoe, Kansas, Millcreek, and Beckjord fly ash. Since all four ashes were composed of complex solid particles and a high concentration of water soluble salts, a number of "model" solids and inorganic salt samples were also utilized as additives for comparative purposes. Four high surface area solids (two silicas and two carbons) were chosen because of their different surface characteristics.

A theoretical approach to the flocculation of a colloidal system involves an understanding of the nature of interactions between suspended particles. In general, dispersed particles remain suspended as long as the repulsive forces operating between particles are greater than their van der Waal's forces of attraction. Since the attractive forces are constant, flocculation can be brought about by reducing the repulsive forces. The two most common types of repulsive forces are: 1) steric hindrance, which can occur when large organic molecules on the particle surface physically prevent the particles from getting close enough together to interact and; 2) coulombic interactions which occur when particles have the same surface charge as a result of electrical double-layer formation. Electrical double-layer predicts that coulombic repulsion will be decreased by increasing the ionic concentration of the system or by decreasing the surface charge. Adding salts to an aqueous system has the effect of increasing the ionic concentration, and is capable of increasing or decreasing the surface charge depending upon the surface properties of the suspended particles. The introduction of insoluble solids to a dispersion can bring about flocculation by interacting directly with the suspended particles, through specific adsorption of ions or molecules, and by destroying the equilibrium conditions which exists across the particle/liquid interface.

The experimental approach was two-fold: 1) an evaluation primarily of the relative effects of various additives on the settling rate of activated sludge, and 2) a determination of the pertinent surface characteristics of the solid additives. The experimental procedure adopted for measuring settling rates had the advantages of utilizing a small volume and of being fast enough so that measurements could be taken in a short period of time before the sludge underwent a radical change in properties. As a result, the effect of several additives could be compared directly on the same batch of sludge. The following surface property information on the

solid additives was obtained by a variety of experimental techniques: 1) specific surface areas; 2) polar surface site concentrations and, to some extent, energetics of these sites; 3) solution adsorption capacity of cationic surfactant dodecyltrimethylammonium bromide, DTAB; and 4) zeta potential at the solid/liquid interface. A relationship was sought between the ability of a solid additive to induce flocculation and its surface properties in order to arrive at a partial mechanism for the improved thickening of activated sludge.

SECTION II

CONCLUSIONS

Various materials added to activated sludge have resulted in a pronounced increase in the settling rate of the solids present in the sludge while other materials have had very little effect on the settleability. The additives which were investigated were separated into the two classifications of solid and water soluble additives in order to permit a more reasonable interpretation of results. The primary additives, which were a fly ash and three sludge incinerator ashes, fall into both categories in that they consisted of both solids and water soluble salts. These ash samples were separated into the above two classifications by washing the solids free of water soluble salts and saving the washings for settleability experiments. The solids utilized as additives in this investigation consisted of magnetite, two carbons: graphon and carbon black Elf-4, and two silicas: Cab-o-sil M-5 and Quso H-40. The water soluble salts consisted of calcium fluoride, aluminum chloride, potassium phosphate, and a series of anionic and cationic polymeric surfactants.

The settleability results, utilizing solids as additives, showed that Elf-4 and Quso H-40 were much more efficient for inducing flocculation in activated sludge than either graphon or Cab-o-sil M-5. Our data indicated that the superior performance of Elf-4 and Quso H-40 is related to their hydrophilic nature and their high concentration of polar groups. Based on these results, the conclusion is that polar surfaces, in a slightly alkaline activated sludge, readily adsorb cationic and polar molecules. The ionic conditions of the solvent and the equilibrium conditions across the sludge particle/liquid interface are thus altered so as to lead to flocculation. Both calcium fluoride and aluminum chloride drastically increased the settleability of activated sludge while potassium phosphate had very little effect. The proposed mechanism of flocculation for the halide additives is that repulsive charge of the sludge particles is effectively eliminated through preferential adsorption of the respective cations, i. e. aluminum and calcium. The fact that potassium phosphate has very little effect on the settleability supports the above mechanism because potassium has a single charge and is weakly acidic as compared to the calcium and aluminum ions which have strong double and triple charges, respectively.

The mechanism which operated when the unwashed ashes were added to activated sludge was somewhat complicated by the complex nature of the ashes themselves. Although a difference in settleability efficiency was detectable for the four unwashed

ashes, as well as the washed solids and washings obtained from the four ashes, this difference was relatively small. Surface property measurements on the washed ashes have indicated that both Lake Tahoe and Millcreek had the most hydrophilic surfaces and both adsorbed twice as much DTAB at a pH of 10, on the basis of per unit area, than Kansas and Beckjord. Also, since Lake Tahoe and Millcreek had higher specific surface areas (17 m^2/g and 7.7 m^2/g, respectively), the washed solids of these two ashes were expected to bring about faster settling rates for activated sludge. The settleability results for the unwashed ashes were in the order: Tahoe > Kansas > Millcreek > Beckjord, while the order for the washed ashes were Kansas > Millcreek > Beckjord > Tahoe.

The most important feature of these results is the reversal of the Tahoe ash from the most efficient before washing to the least efficient after extensive washing. Since the results cannot be explained in terms of extent of surface area, particle size, or concentration of water soluble salts even after washing, it must be concluded that the anomalous behavior of this ash can only be elucidated by further investigation of its surface properties in the sludge liquid environment. A general mechanism, however, has been postulated whereby the sludge solids are assumed to have a negative charge and increased settling rate is brought about by bridging of the solid additive particles of low negative or positive charge and/or by adsorption of cationic surfactants on the sludge solids, which leads to a direct interaction and flocculation of sludge particles.

SECTION III

RECOMMENDATIONS

The results of this investigation have shown that both inorganic salts and solid additives are capable of inducing flocculation in activated sludge and improving its ability to be dewatered. From these results a mechanism was postulated for the ability of ash to condition waste activated sludge. Furthermore, a relationship was found between the surface properties of the solid additive and its ability to induce flocculation. Several mechanisms were proposed to explain the behavior of the various additives. The authors feel that with this knowledge and experience now available, more intensive research should be pursued to obtain specific information on the interactions involved in the proposed mechanisms. Concerning the solid additives, the approach should be to study their interfacial properties in the supernatant of the activated sludge. This could be accomplished by electrophoresis, conductivity and pH measurements, as well as by solution adsorption measurements of various surfactants and polymers. The effects of salts on the settleability of activated sludge should be investigated as a function of valency and ionic strength. Finally, and by far the most difficult recommendation, the interfacial properties of the activated sludge particles themselves should be investigated after exposure to the various additives. The objectives of these recommendations is to increase our knowledge of the specific nature of the interactions which lead to flocculation and to evaluate more efficient methods for practical applications of waste water treatment.

SECTION IV

EXPERIMENTAL

The activated sludge was obtained from the extended aeration plant at Allentown College of St. Frances De Sales, Upper Saucon Township, Lehigh County. One of the advantages of this source of activated sludge is its close proximity to our laboratories - it is located 2 miles from Lehigh University. Furthermore, College life tends to be somewhat more "regimented" and hence, hopefully, a more consistent sewage and sludge are generated. Nevertheless, experience has shown that the percent of solids present can vary during periods of heavy rainfall and when the students are on vacation. For example, the percent of solids appears to always be less than 0.20% on Monday mornings. In general, settleability results are presented only when the solid concentrations were between 0.20% and 0.25% with volatile concentrations varying between 80% to 85%.

The ashes used in this study are identified as follows:

1. Tahoe - Lake Tahoe ash, produced by the incineration of a combination of primary, secondary and lime tertiary sludges.

2. Kansas - Kansas City ash, produced by the incineration of a raw-primary sludge. The source for this ash was the Blue River sewage treatment plant in Kansas City, Mo.

3. Millcreek - Millcreek incinerator ash, produced by the incineration of a raw-primary sewage sludge. This Millcreek sewage works is the main treatment plant in Cincinnati.

4. Beckjord - Beckjord ash, which is the fly ash resulting from the combustion of coal for the production of electric power. This plant produces much of the electric power required in the Cincinnati area.

The particle size distribution of the ashes was determined by standard dry sieve analysis. This method was also used to separate the various size fractions for further analysis.

The various ash powders were analyzed for their composite materials by means of an X-ray diffraction technique, and measurements were recorded with a Norelco type 42771 Geiger-counter Diffractometer. The X-ray emission was generated from an iron target with a manganese foil filter at 40 kilovolt and 10 millamperes. By means of automatic recorders integrating the Geiger counts at continuously varying angles, the characteristic ash-powder pattern appeared as a series of peaks on a continuous background. The spacings and intensities of the peaks obtained from the unknown ashes were subsequently compared to reference patterns of known materials for identification.

A number of inorganic oxides and carbon blacks, whose surface properties had been characterized to some extent in the literature, were investigated for their efficiency as flocculants for activated sludge. The primary samples studied were two silicas: Cab-o-sil M-5 (Cabot Corporation) made by the vapor phase hydrolysis of silicon tetrachloride at 1100°C, and Quso H-40 (Philadelphia Quartz Co.) which is a precipitated silica; and two Cabot Corporation carbon samples: Elf 4 which is a commercial grade channel carbon black and graphon which is Elf 4 graphatized at 2700°C.

The solution adsorption isotherms of the cationic surfactant dodecyltrimethyl-ammonium bromide, DTAB, were measured by a technique previously used by Barr, Oliver and Stubbings [9]. The procedure for analysis was to titrate the DTAB solution against a standard solution of sodium dodecylsulphate, SDS, in the presence of bromophenol blue (as indicator) and chloroform. Any excess of DTAB interacted with the indicator to produce a blue-colored complex which was soluble in chloroform. The endpoint of the titration was indicated by transition of the blue color from the aqueous to the chloroform layer. The reaction between the two surfactants was not completely stoichimetric, but the deviation, which was less than 5%, was reproducible.

The settleability of activated sludge was determined by placing 25 ml of sludge in a 15 cm-long test tube and measuring the position of the boundary between solids and clear supernatant as a function of time. Due to the possibility, and ultimate probability, of the nature of the sludge changing with time, the procedure adopted was to have four people make measurements simultaneously. In this way, a minimum of 16 determinations could be carried out during a 1-hour period. Reproducibility was found to be excellent during this time period. The duration of the experiment was limited to 10 minutes because it was found that if the settling did not occur in this time, then the suspension remained stable for long periods.

SECTION V

CHARACTERIZATION OF SOLID ADDITIVES

The characterization of the surface properties of solid additives, including carbon and silica as well as ash samples, is very important for an understanding of the mechanism whereby these materials induce flocculation in activated sludge systems. Although a variety of approaches have been utilized in this study to characterize the surfaces of the different samples, some problems were encountered with the ash samples. Nevertheless, the direct comparison between the well characterized carbon and silica surfaces and the ash surfaces represents a powerful tool for explaining the improved solids-liquid separation of ash conditioned waste activated sludge.

The ash samples, as received, contained a wide particle size distribution. Standard dry sieve analysis procedures were used to measure the particle size distribution and to separate different size fractions for further experiments. The results given in Figures 1 and 2 for the four ashes show that the particle size varies from the submicron range to about 5 mm. Two facts are immediately evident from these results. The Beckjord fly ash has the smallest particle size distribution with a majority of the particle being less than 250 microns and a significant fraction less than 38 microns, while Lake Tahoe incinerator ash has the largest particle size distribution with a majority of the particles exhibiting a diameter greater than 250 microns.

The BET surface areas of the ash samples were measured by two methods: 1) a volumetric method utilizing N_2 as the adsorbing gas and 2) a gravimetric method utilizing Ar as the adsorbing gas. The results are given in Table 1 for the four ashes. It should be noted that the N_2 areas were measured on the unwashed ashes while the Ar areas were measured on ash samples which had been washed extensively. In general, Ar and N_2 surface areas should yield the same results. The washed and unwashed samples, however, can be expected to give different results when appreciable amounts of water soluble material are present on the surface. Taking these factors into consideration, the N_2 and Ar areas presented in Table 1 show reasonably good agreement. The surprising feature which emerges from the surface area results is that Beckjord fly ash, which has the smallest particle size distribution, exhibits the smallest surface area, 1.6-1.8 m^2/g, and Lake Tahoe incinerator ash, which has the largest particle size distribution, exhibits the highest surface area, 11.5-17 m^2/g. Nevertheless, all of the ash

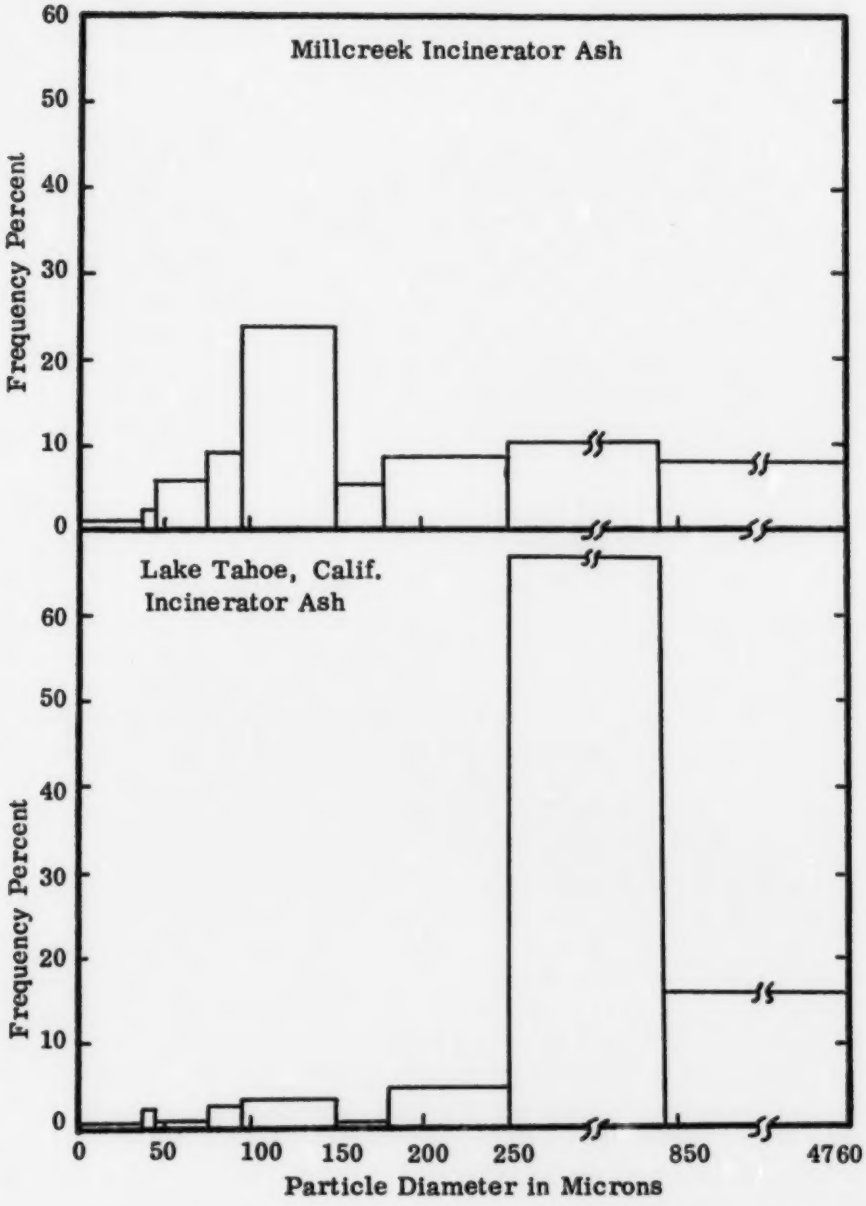

Figure 1 - Particle Size Distribution of Millcreek and Lake Tahoe Incinerator Ashes.

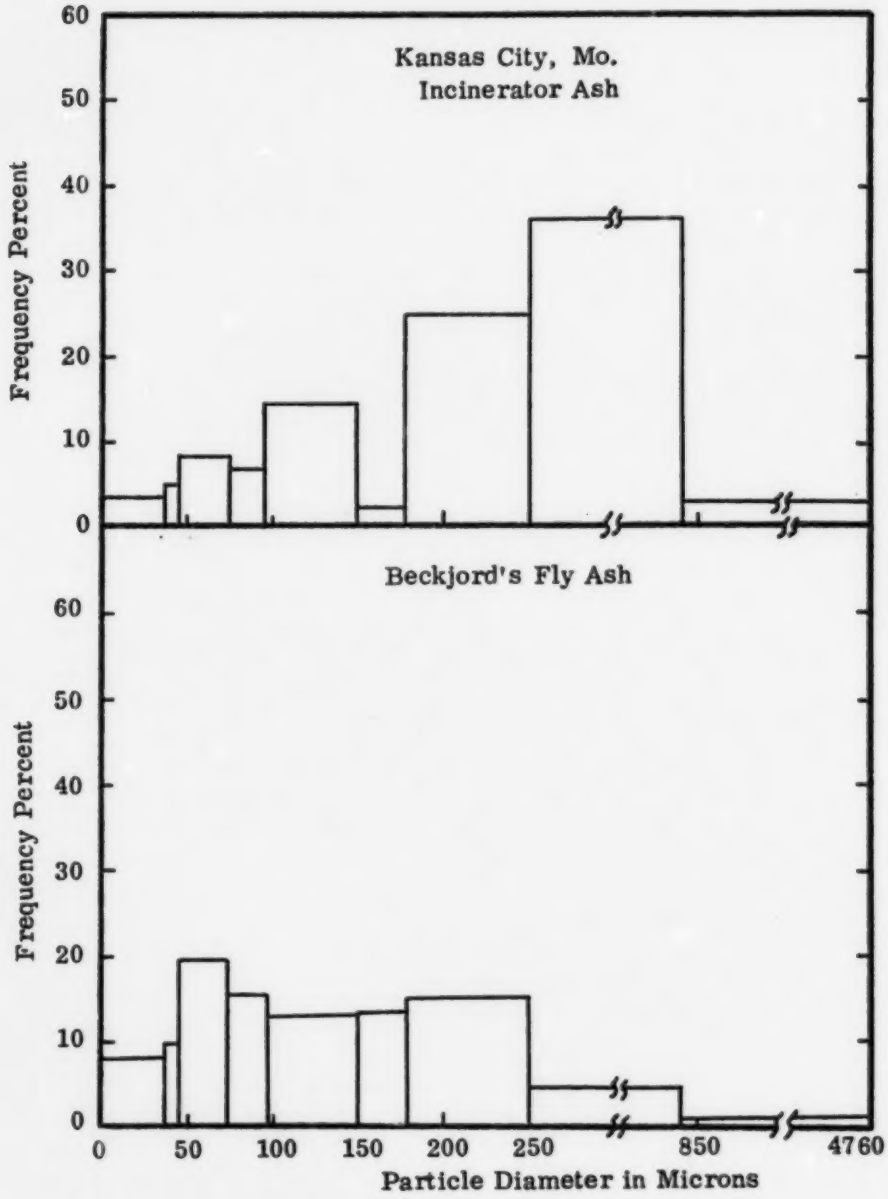

Figure 2 - Particle Size Distribution of Beckjord Fly Ash and Kansas Incinerator Ash.

samples are porous to some degree since the surface area range of the ash sample, i. e. 1.6-17 m^2/g is indicative of uniform spheres with diameters in the range of 1 to 20 microns.

Table 1. BET Surface Areas of Ash Samples

Sample	Size Fraction	N_2 Area of Unwashed Ash, m^2/g	Ar Area of Washed Ash, m^2/g
Kansas	Complete	3.4	2.7
Millcreek	Complete	7.0	7.7
Tahoe	Complete	11.5	17.0
Beckjord	Complete	1.6	1.8
Beckjord	38 microns	0.5	---
Beckjord	250-840 microns	4.5	---

The X-ray diffraction patterns for Kansas, Lake Tahoe and Millcreek incinerator ashes are given in Figure 3 along with the diffraction patterns for some reference standards. Quartz shows signs of being present in all three ashes. Fluor-apatite and Lewistonite both have the same reference diffraction patterns and appear to be present only in the Lake Tahoe ash. Both the Fluor-apatite and Lewistonite contain sodium, potassium and phosphate ions while Fluor-apatite also contains fluoride and calcium. The Tahoe ash, which did exhibit some magnetic properties, shows some signs of containing Magnetite. Figure 4 gives the X-ray diffraction patterns for the small and large particle size fractions of Beckjord Fly Ash. The large particle size fraction of Beckjord exhibited magnetic properties while the small fraction contained about 50% of material which was also attracted to a magnet. The small particle size fraction, therefore, was further separated by means of a magnet for X-ray analysis. The results in Figure 4 show that quartz was probably present in all three fractions of Beckjord. Although the definition of peaks above $2\Theta = 50°$ was poor for the large particle size fractions, the primary quartz peak was detectable at $2\Theta = 32°$. Magnetite was apparently present in the large particle size and the fine particle size fraction which exhibited magnetic properties. A number of metal oxides were tested and found not to be present in any of the four ash samples.

The water soluble ions on the surface of the ash samples were determined by placing 25 mg of ash in 25 ml of deionized water and measuring the pH and conductivity of the solution. The results of these experiments, which were measured as a function of particle size, are given in Figure 5. The Kansas City, Lake Tahoe and Millcreek ashes all exhibited very little variation in pH and conductivity as a

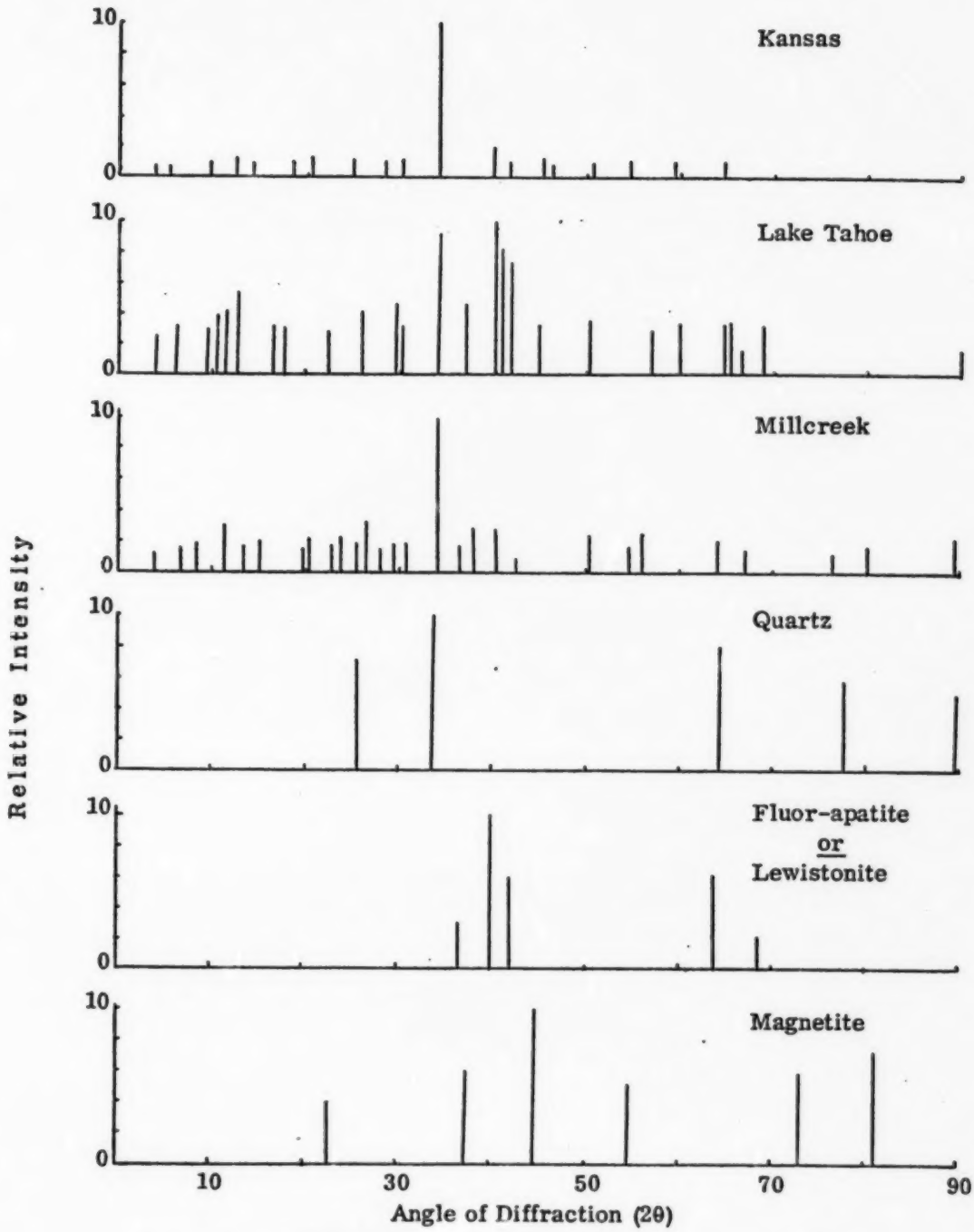

Figure 3 - X-Ray Diffraction Pattern of Incinerator Ashes and Reference Standards.

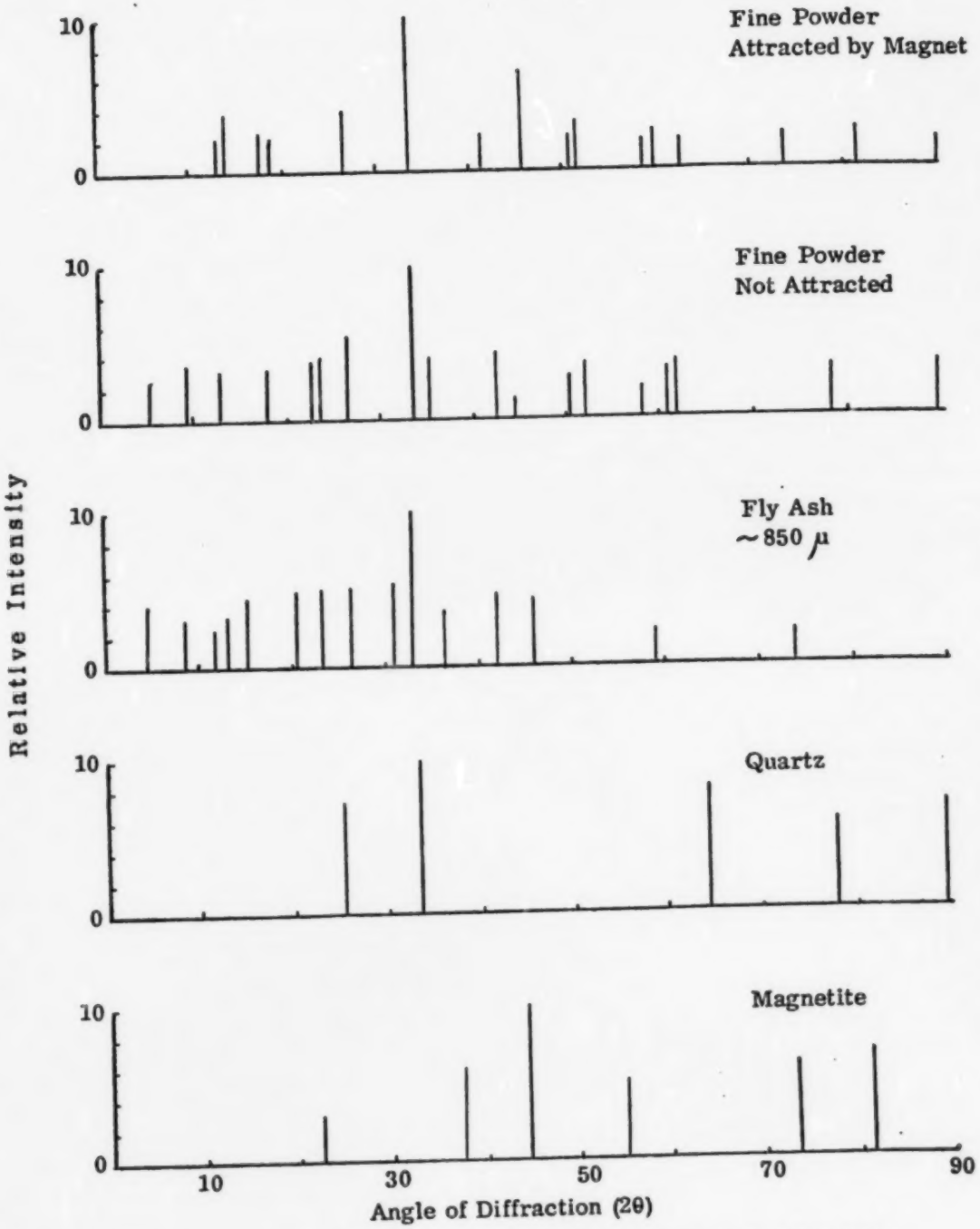

Figure 4 - X-Ray Diffraction Pattern of Beckjord's Fly Ash and Reference Standards.

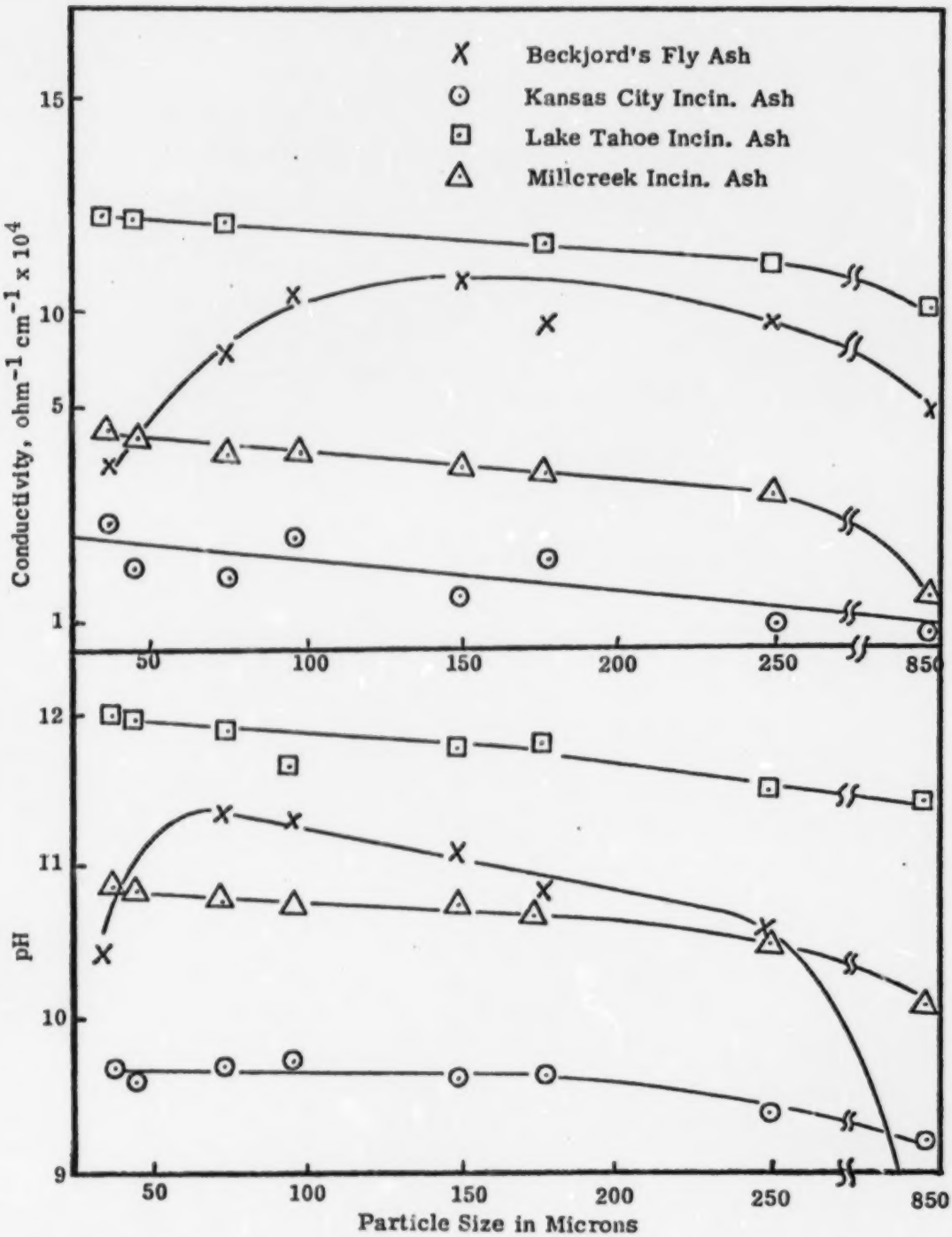

Figure 5 - Conductivity and pH of Ash Dispersion as a Function of Particle Size.

function of particle size. In general, the conductivity and the pH decreased with increasing particle size. The Beckjord fly ash, however, showed rather anomalous behavior in that the conductivity and pH initially increased followed finally by a decrease, with increasing particle size. The conductivity for all four ashes fell within the range of 1×10^{-4} to 2×10^{-3} mhos cm^{-1} while the pH varied from 9 to 12. The only exception was the particle size fraction of Beckjord greater than 840 microns which resulted in an acid solution with a pH of 3.7. These results suggest that the surface of the Beckjord fly ash below 97 microns and greater than 840 microns is very much different from the intermediate size material.

The pH and conductivity for the particle size fraction less than 38 microns for all four ashes was followed as a function of the number of washings in order to determine the absolute concentration of water soluble salts present in each sample. The results, which are given in Figures 6 and 7, show that the Beckjord and Kansas City ashes are washed to constant pH and conductivity with less than 20 washings. The Lake Tahoe and Millcreek ashes, however, both have a pH which appears to level off at 9.5 after 20 washings and retain a surprisingly high conductivity. The high degree of porosity which was found for the Lake Tahoe ash could be responsible for these results.

Figure 8, a and b, show the variation of conductivity and pH, respectively, of 50 mg of total ash in 25 ml of de-ionized water as a function of time. The samples were stored in closed containers and frequently agitated. The plot of conductivity (representing total ionic species present) against time is of the expected form, i.e. the conductivity increases with increasing time. The results of pH vs. time, however, is interesting for all four ashes because the pH first increases followed by a slow decrease. Apparently the ashes contain mixtures of water soluble species, both of acidic and basic character, which have different rates of solubility. The acidic species appear to dissolve much more slowly than the basic species.

Figure 9 gives the values of equilibrium pH as a function of total ash concentration in both de-ionized water and activated sludge. These results show that Lake Tahoe contains the highest concentration of basic ions, followed by Millcreek, Beckjord and Kansas. The most pronounced difference is in activated sludge, which tends to act as a buffer to lower the pH, where Lake Tahoe increases the pH even at low ash concentrations.

Water and isopropanol gas adsorption measurements were carried out on two silicas and two carbons, as well as on the four ashes of primary interest. These experiments must be considered preliminary because of the limited amount of work devoted to this area. The reason for investigating the solid/gas interfacial properties was to characterize the surface with respect to polar site concentration and homogeneous nature of the surface. This information can frequently be invaluable for understanding solid/liquid interactions [6]. Figure 10 gives the water adsorption results for two silicas, Cab-o-sil M-5 and Quso H-40, and two carbons, carbon black Elf 4 and graphon. The abscissa axis gives the relative pressure of the water

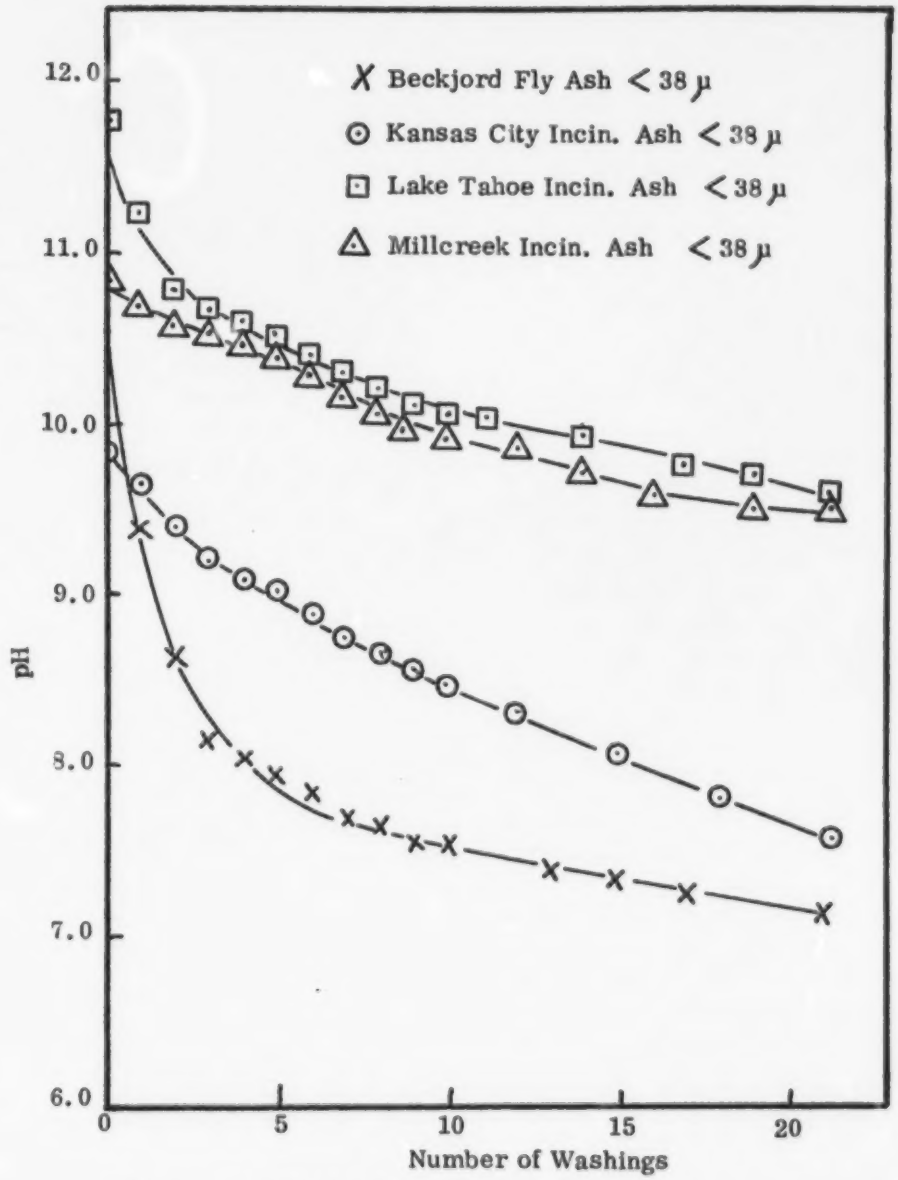

Figure 6 - pH of Ash Dispersions as a Function of Number of Washings.

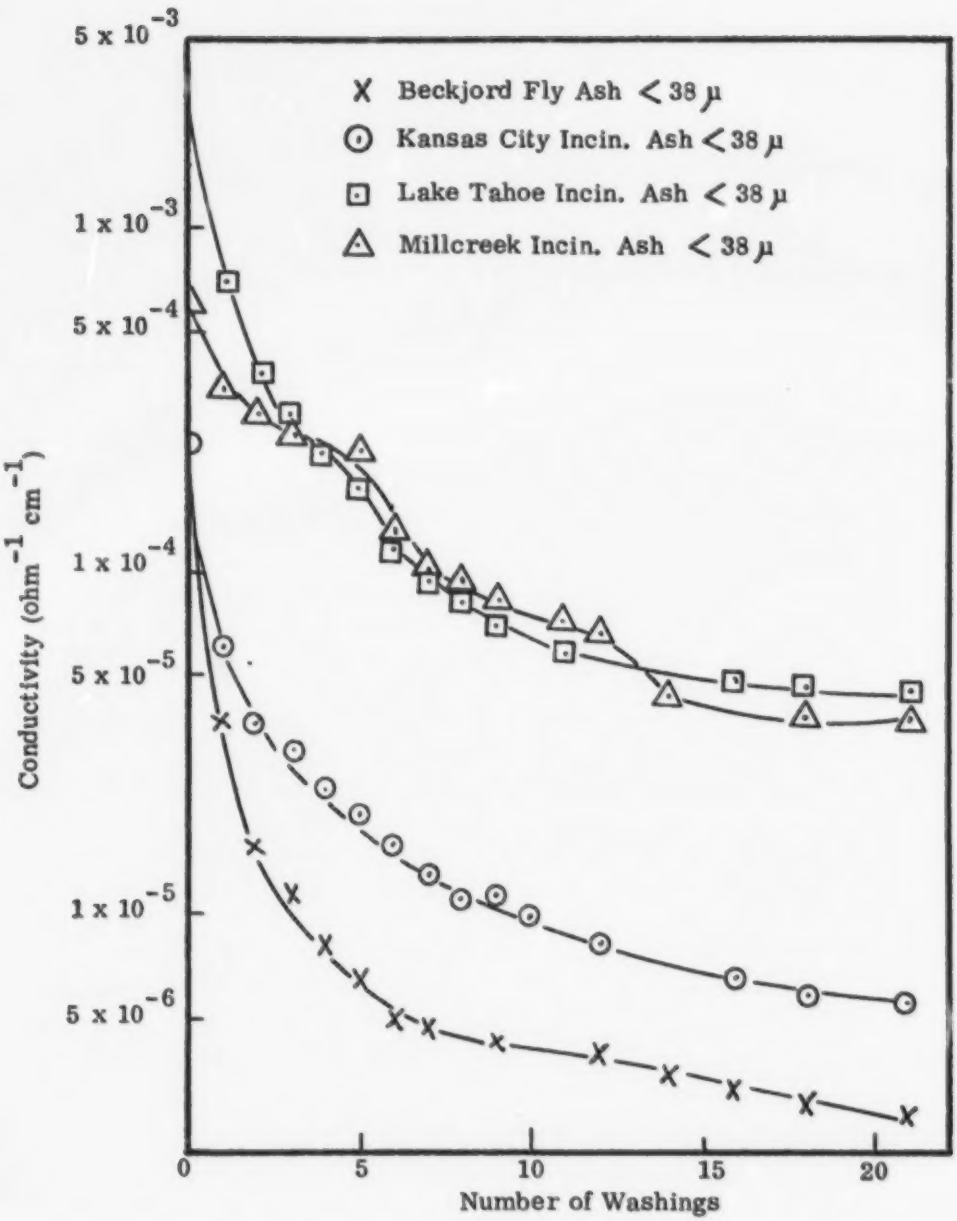

Figure 7 - Conductivity of Ash Dispersions as a Function of Number of Washings.

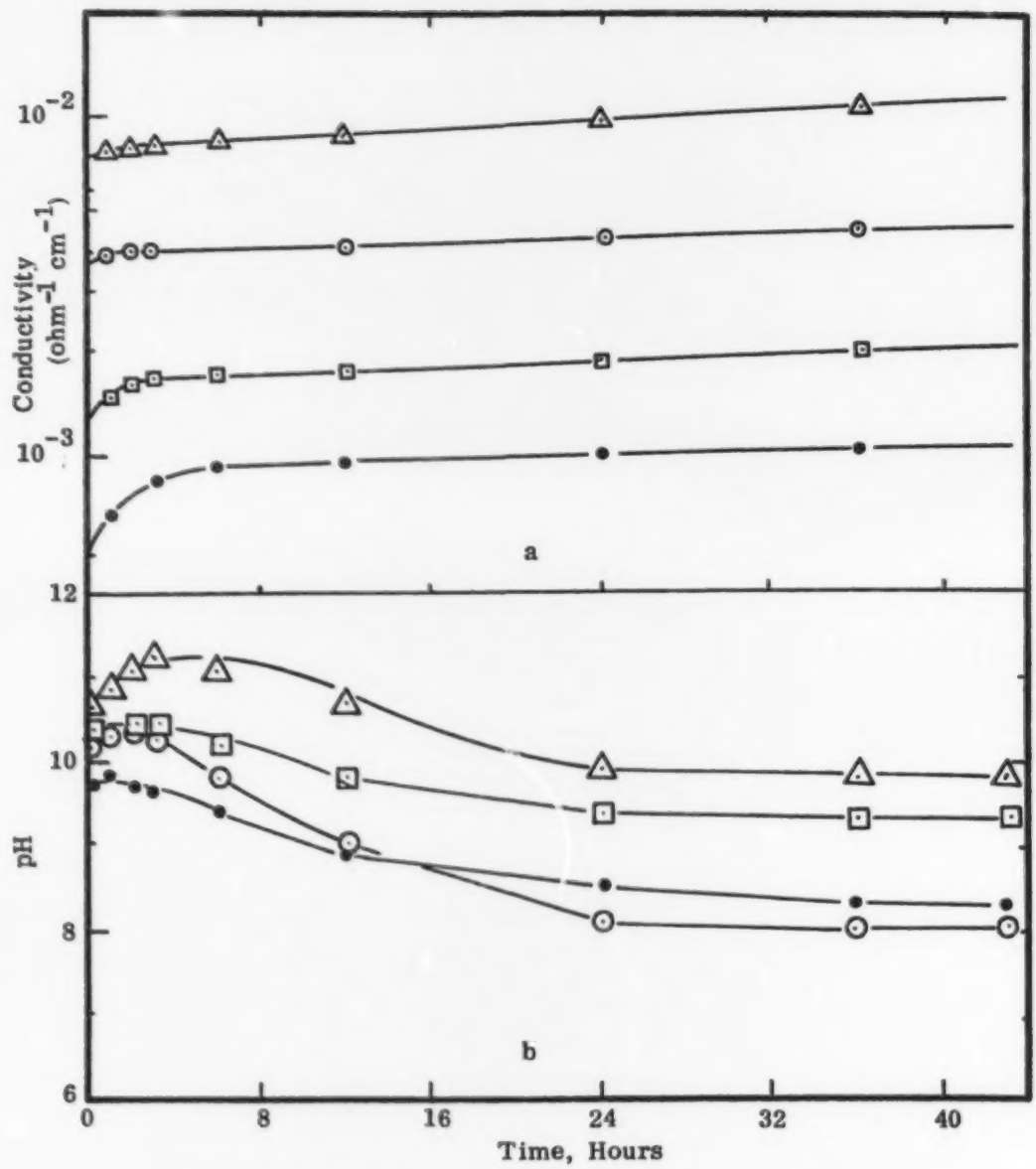

Figure 8 - a) Conductivity and b) pH of Total Ash Dispersions as a Function of Time.

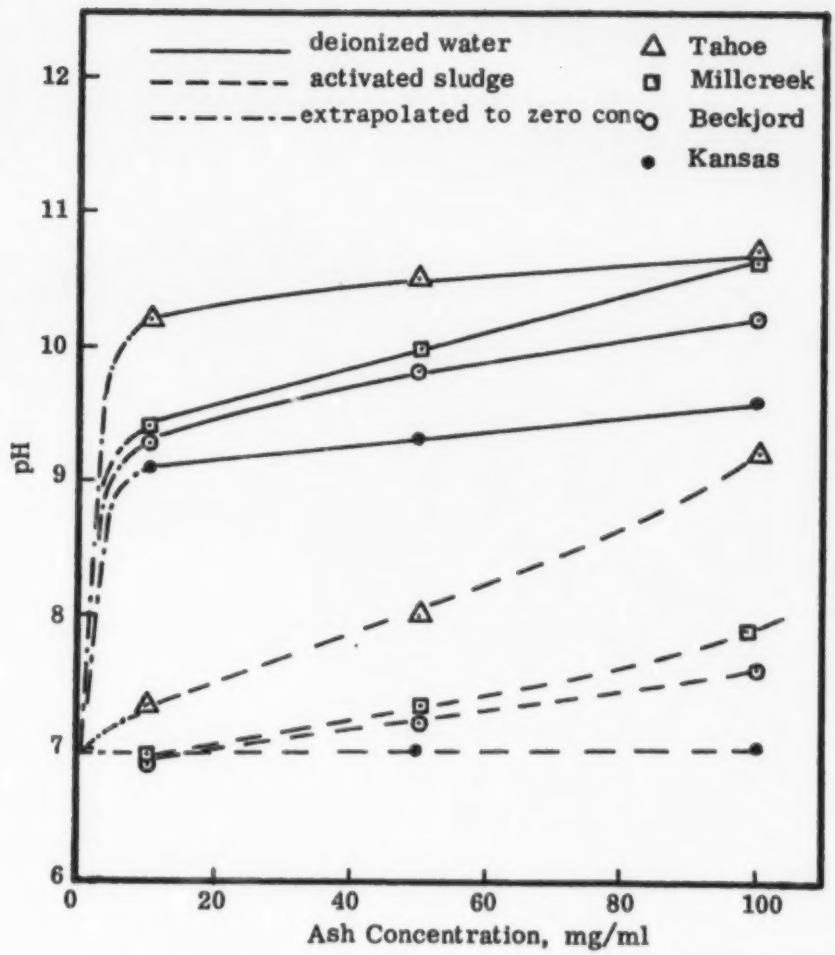

Figure 9 - pH of Total Ash Dispersions as a Function of Concentration in Deionized Water and Activated Sludge.

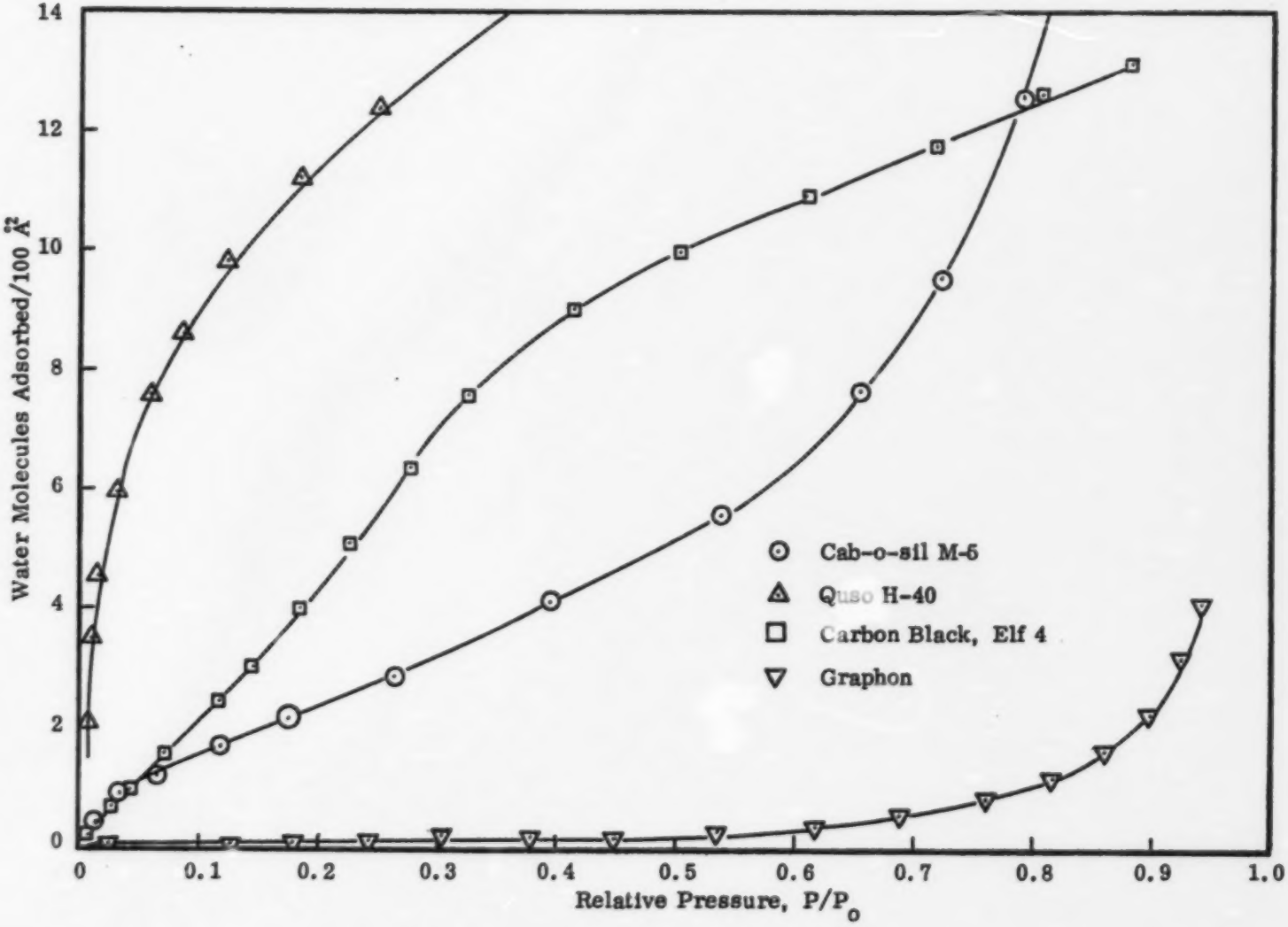

Figure 10 - Water Adsorption Isotherms on Silica and Carbon Surfaces.

vapor at equilibrium with the sample and the ordinate axis gives the number of water molecules adsorbed per 100 $\AA^2$ (based on a BET argon surface area). A close packed monolayer of water would theoretically be expected at a coverage of 10 molecules/100 $\AA^2$. Ordinarily a nominal monolayer is determined from an isotherm by noting the level of adsorption which occurs at the inflection in the isotherm. Both Quso and Cab-o-sil exhibit inflections at a relative pressure of about 0.1 and a coverage of 11 and 1.5 molecules/100 $\AA^2$, respectively. The interpretation is that Quso is a hydrophilic surface with a high concentration of surface hydroxyl groups and Cab-o-sil is a hydrophobic surface with a low concentration of surface hydroxyl groups. Carbon black Elf 4 shows evidence of a small inflection at 1 molecule/100 $\AA^2$ and a larger inflection at 10 molecules/100 $\AA^2$. Since it is known that carbon blacks are hydrophobic, amorphous surfaces [7], the first inflection is attributed to a low concentration of polar organic groups on the surface, and the complete adsorption, as evidenced by the second inflection, is due to low energy adsorption on imperfection sites. Graphon, however, has no surface functional groups and exhibits well defined X-ray diffraction patterns [7]. The results in Figure 10 show very little adsorption for graphon and thus indicate that graphon is 100% hydrophobic. The fact that all four surfaces exhibit entirely different surface properties is not accidental, but rather is the reason why they were chosen as additives for activated sludge systems.

Gas adsorption measurements on the incinerator ashes and fly ash were not as straightforward, experimentally as those obtained for silica and carbon samples. The initial isotherms, which were measured on unwashed samples, were not reproducible and the isotherms were not reversible. Extensive washing of the ash samples increased both the reproducibility and the reversibility of the water isotherms. Nevertheless, the results suggest that more extensive treatment, including high temperature activation, could yield different results and increase our knowledge of these complex ash surfaces. The water adsorption isotherms for the four washed ashes are presented in Figure 11. All four water isotherms exhibit shapes which are similar to the silica results, Figure 10, but the levels of adsorption are much higher for the ash samples. Millcreek absorbs the most water with an isotherm inflection at 30 molecules/100 $\AA^2$ followed by Lake Tahoe, Beckjord and Kansas with an inflection at 18 molecules/100 $\AA^2$. These high levels of adsorption at low relative pressures can be due to the filling of micropores or to the formation of water complexes with water soluble salts, which were not completely removed by numerous washings. In general, the shape of these four isotherms are more closely approximated by the silica water adsorption isotherms.

The isopropanol adsorption isotherms measured on the silica and carbon samples are presented in Figure 12. Although all four samples exhibit levels of adsorption which indicate complete coverage of the surface, i.e. 3-4 molecules/100 $\AA^2$, the number of molecules adsorbed at low relative pressures is significantly higher for the silica surfaces than for the carbon surfaces. These results indicate that isopropanol adsorbs onto the surface silanol sites with a higher energy of inter-

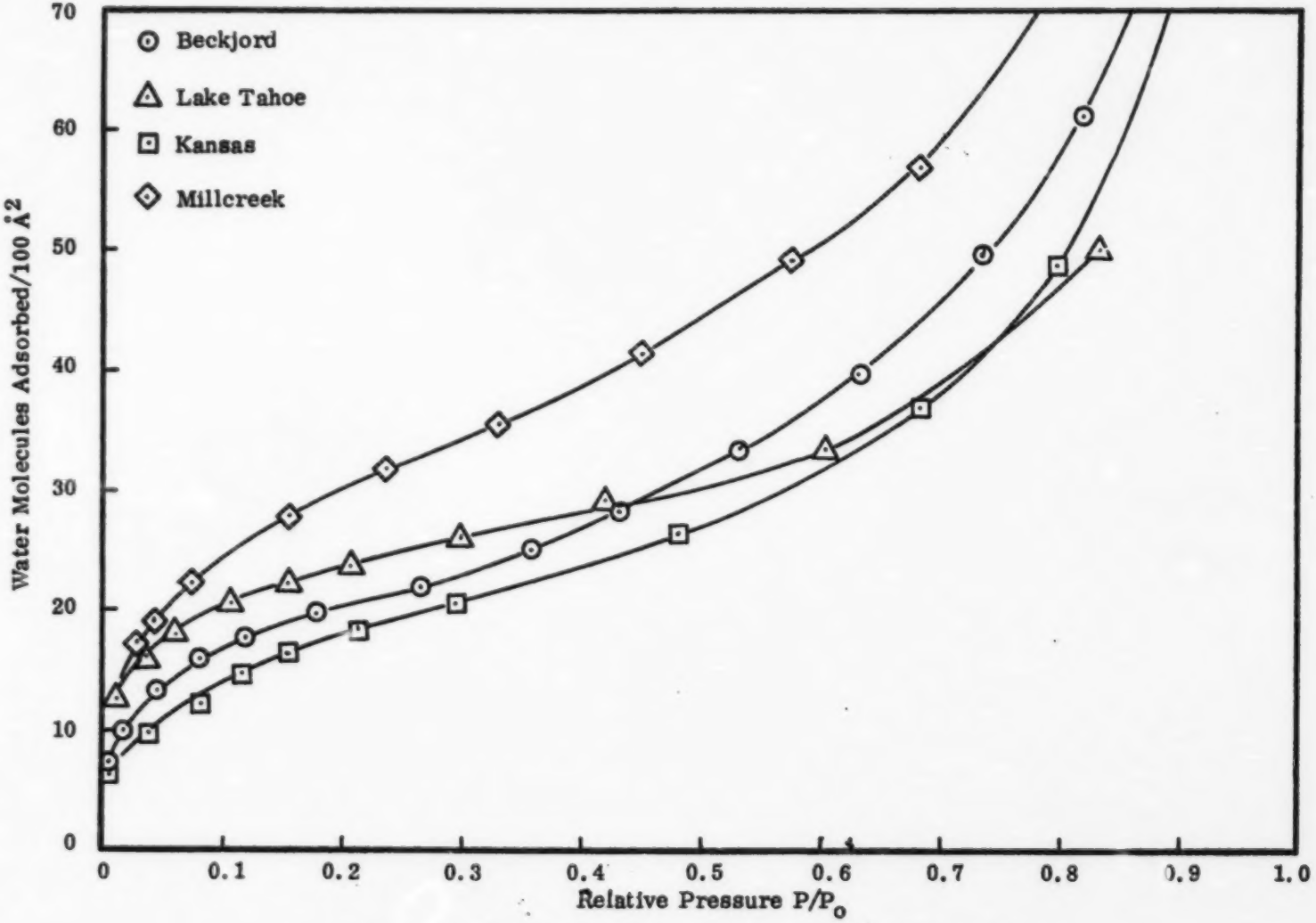

Figure 11 - Water Adsorption Isotherms on Total Ash Samples.

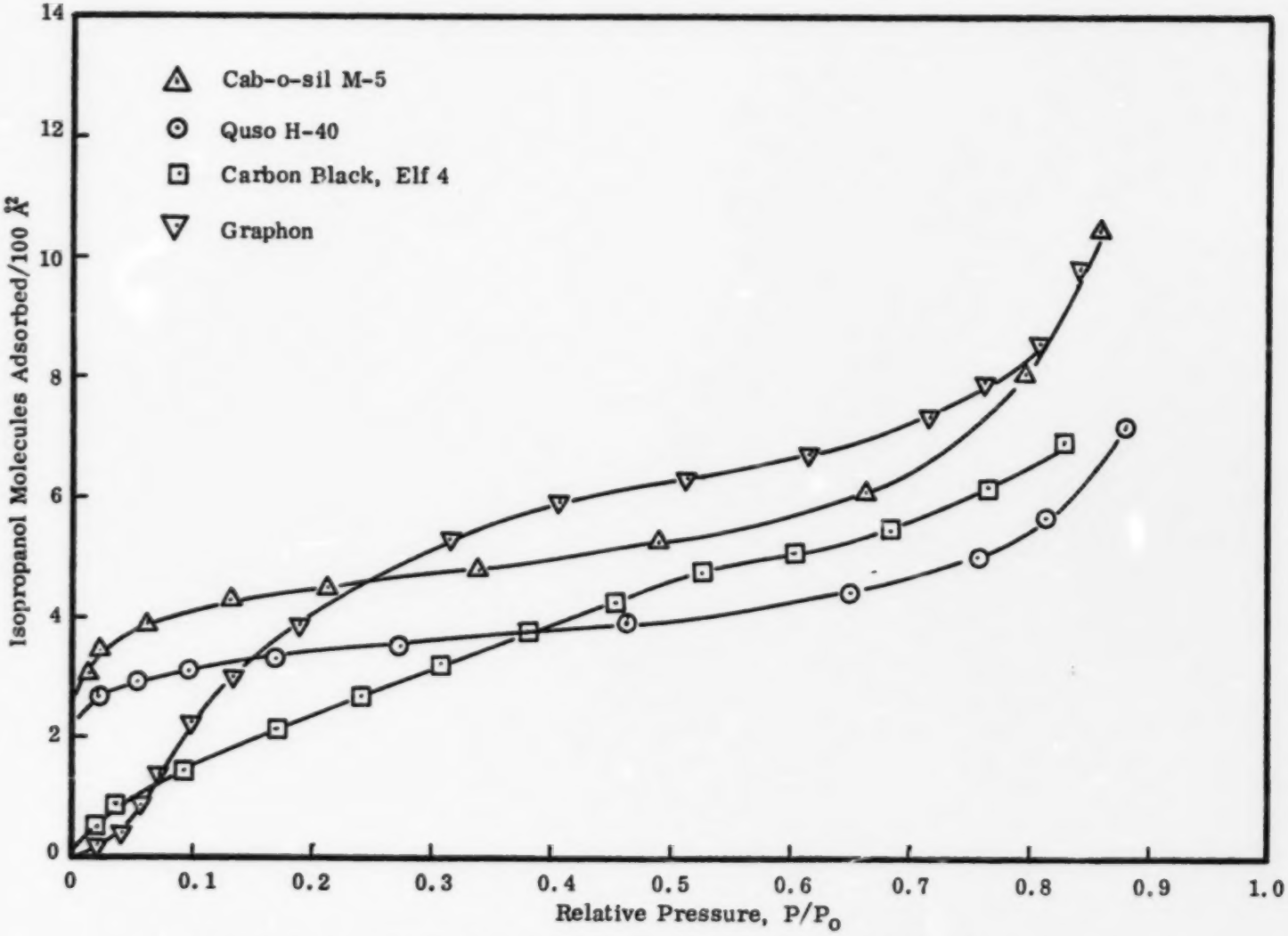

Figure 12 - Isopropanol Adsorption Isotherms on Silica and Carbon Surfaces.

action than with the amorphous surface sites of carbon black Elf 4 or the graphitized surface of graphon. The isopropanol adsorption isotherms on the total ash samples are given in Figure 13. The shape and level of adsorption for all three incinerator ashes, Lake Tahoe, Kansas City and Millcreek, closely approximate the isopropanol adsorption isotherms obtained on the silica samples. The Beckjord fly ash isopropanol isotherm, however, exhibits some characteristics of a carbon surface in that the amount adsorbed increases appreciably over the relative pressure range of 0.1 to 0.6. Apparently an appreciable amount of carbon is present on the fly ash surface.

Solution adsorption isotherms of dodecyltrimethylammonium bromide (DTAB), which is a cationic surfactant commonly used as a softener in laundry processes, were measured on carbon, silica, and the four ash samples. Figure 14 gives the solution adsorption results for Elf 4 and graphon at pH = 11 and pH = 7. At pH = 11, the ionic intermolecular repulsion of DTAB molecules is reduced so that a maximum packing of 3.9 molecules/100 $\AA^2$ occurs on both carbon surfaces. When the pH $\leq$ 7, ionic repulsion between molecules is pronounced and the adsorption configuration becomes important. Adsorption on graphon is expected to occur primarily through the hydrocarbon chain while adsorption on Elf 4 can occur by way of both the hydrocarbon chain and the polar functional group with the hydrophilic sites. The results, Figure 14, show that Elf 4 reaches a maximum adsorption of 2.7 molecules/100 $\AA^2$ compared with 1.8 molecules/100 $\AA^2$ for graphon. This difference is primarily attributed to the hydrophilic sites present on the Elf 4 surface. The same mechanism can be observed on the silica surfaces at pH = 7.5, Figure 15, where Quso H-40 exhibits a maximum adsorption of 3.6 molecules/100 $\AA^2$ compared with 0.6 molecules/100 $\AA^2$ for Cab-o-sil M-5 which was observed from gas adsorption measurements to have a much lower hydrophilic site concentration. The pH = 11 results on silica show that Quso H-40 achieves maximum close packing of DTAB, i.e. 3.9 molecules/100 $\AA^2$, while Cab-o-sil M-5 adsorbs only 2.4 molecules/100 $\AA^2$. Apparently the hydrophobic matrix of Cab-o-sil M-5 adsorbs very little DTAB, if at all.

The solution adsorption results of DTAB on washed ash samples are given in Figures 16 and 17 as a function of the amount adsorbed per gram and per unit area of sample, respectively. Although Figure 16 is useful for determining charges which might take place in an activated sludge system, only Figure 17 can be used to evaluate the surface properties of the solid/liquid interface. Apparently, Lake Tahoe and Millcreek have a higher adsorptive capacity for the cationic DTAB than Kansas and Beckjord. The higher adsorption of DTAB can be due to a higher surface charge density at the higher pH, a greater concentration of surface polar sites, or a steric effect due to pores. A more detailed interpretation of these results will be made later in this report.

Table 2 also presents the electrophoretic mobility, the Ue, of both the washed and unwashed ashes in distilled water, as well as the results after the ashes

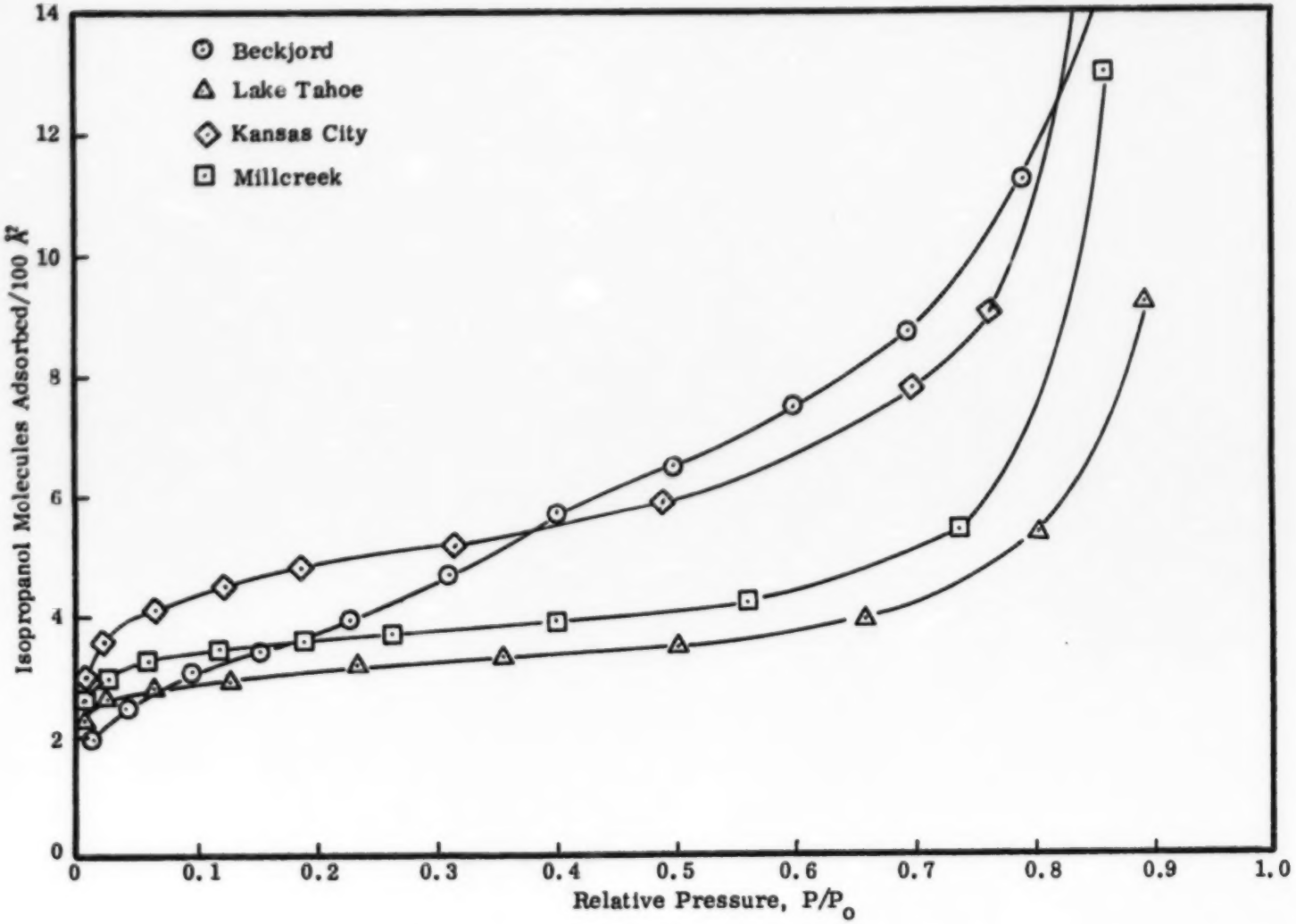

Figure 13 - Isopropanol Adsorption Isotherms on Total Ash Samples.

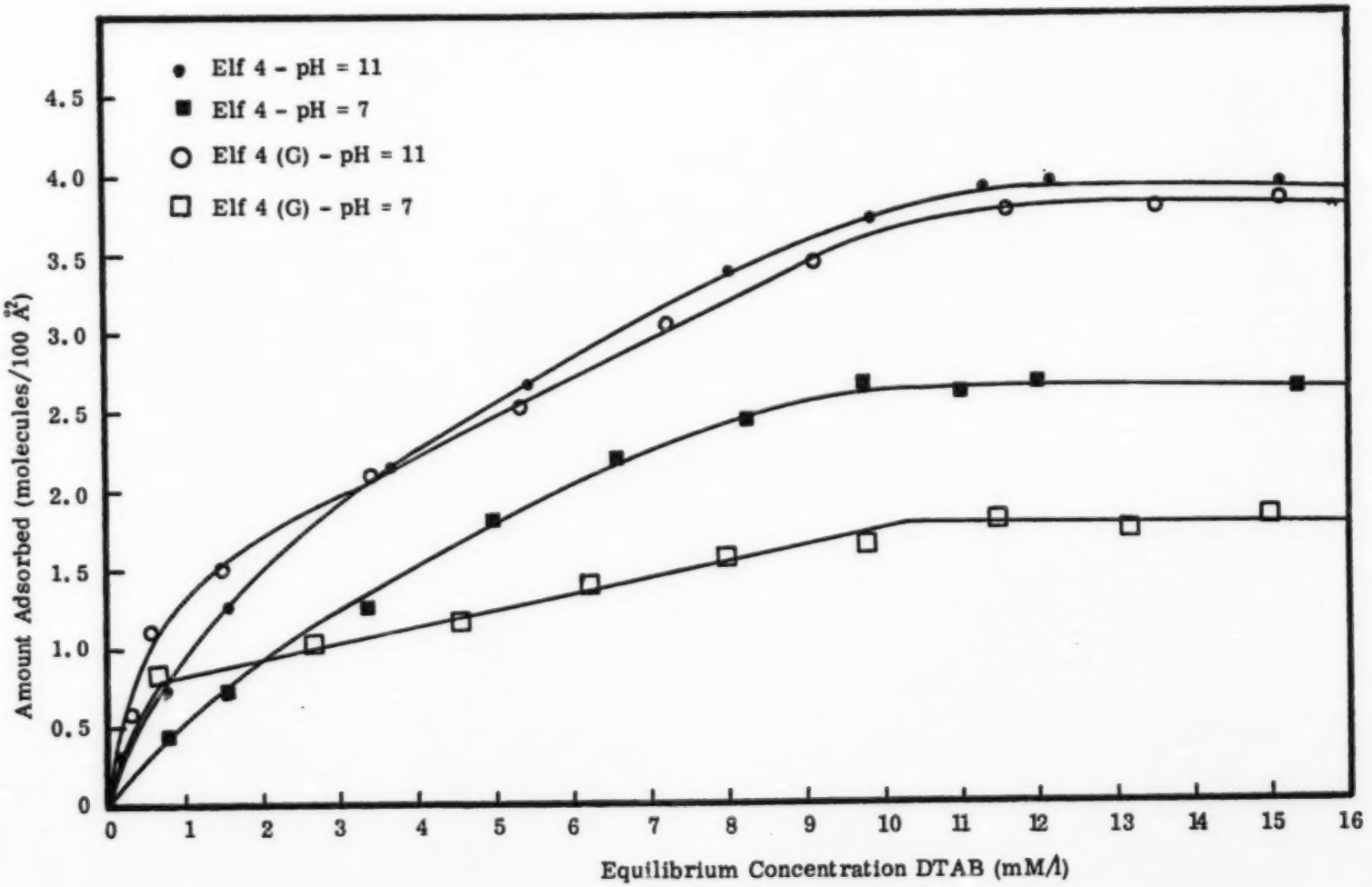

Figure 14 - Adsorption of DTAB onto Carbon Surfaces.

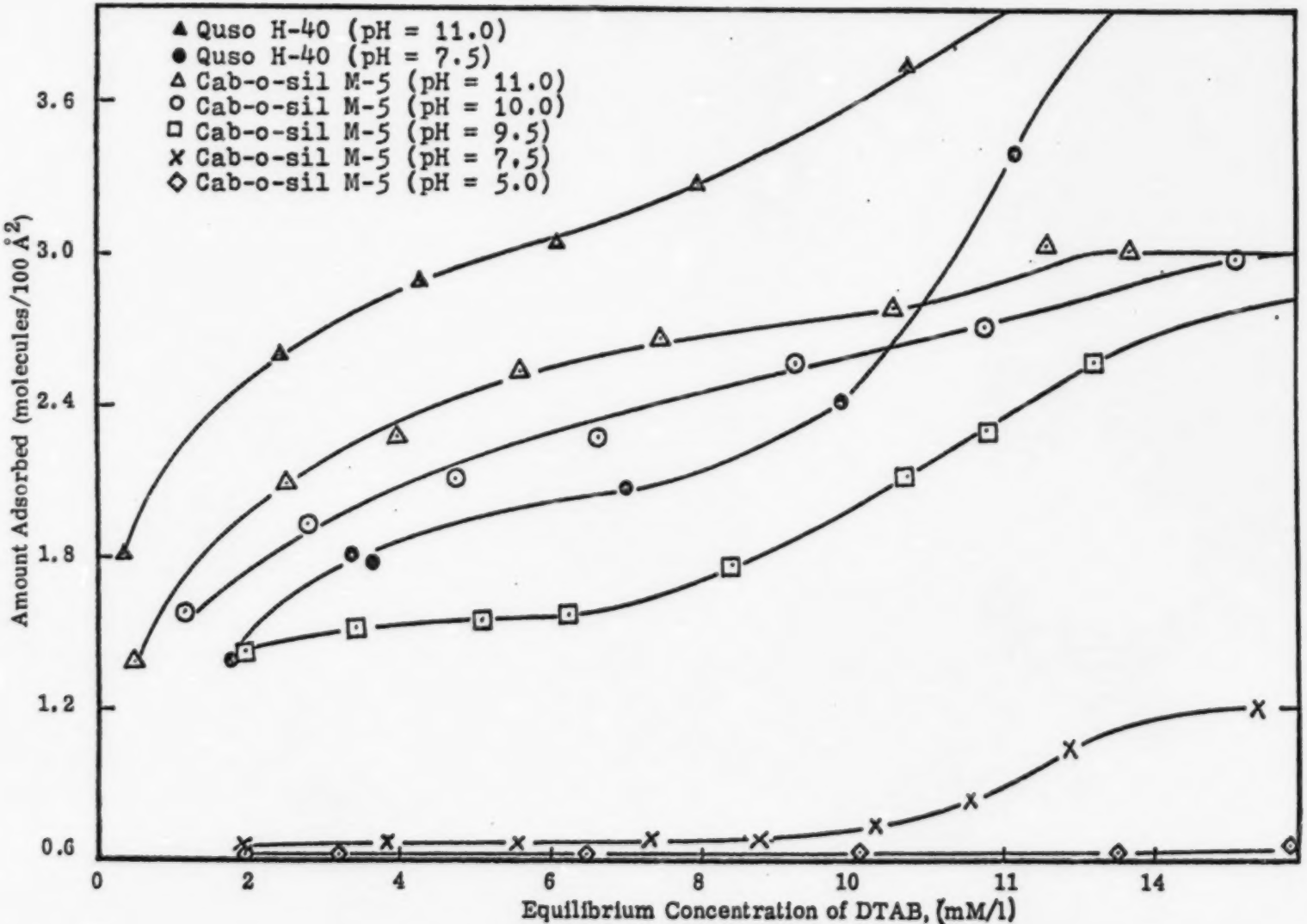

Figure 15 - Solution Adsorption on Silica.

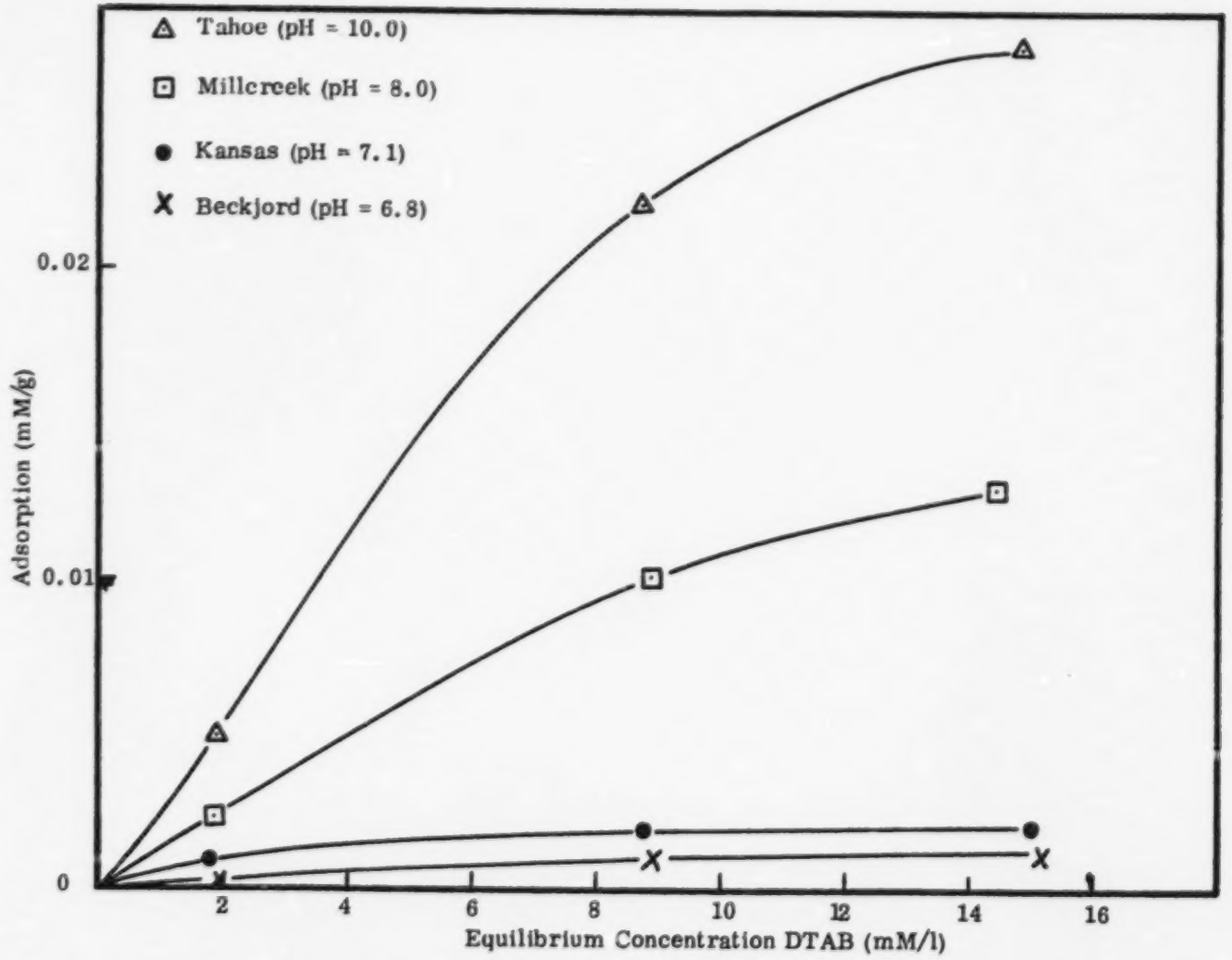

Figure 16 - Solution Adsorption of DTAB Onto Ash Samples in Units of Millimole Per Gram.

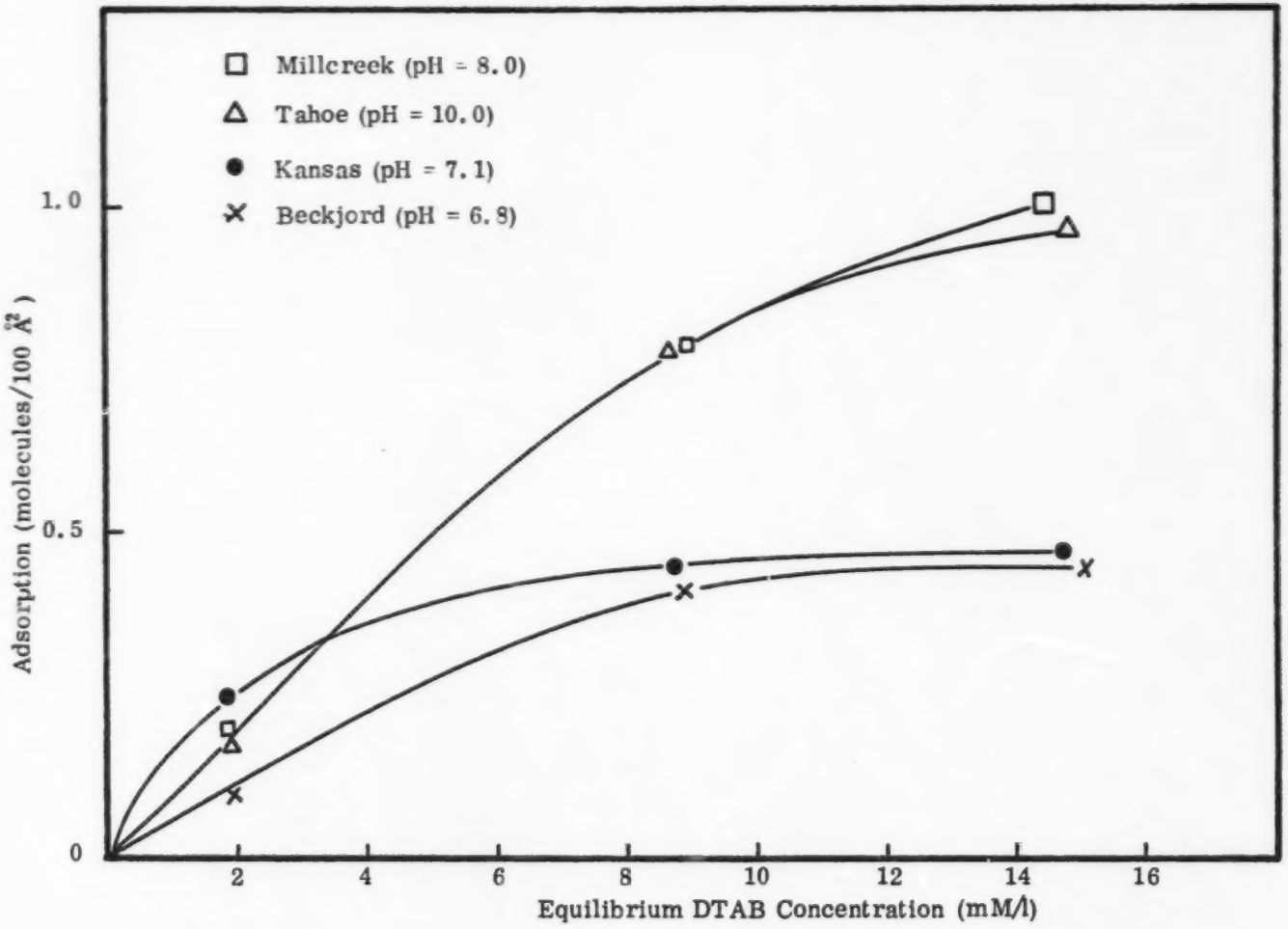

Figure 17 - Solution Adsorption of DTAB Onto Ash Samples in Units of Molecules per 100 Å^2.

Table 2. Surfactant Solution Adsorption and Electrophoretic Mobility of Ash Samples

		Distilled Water		15 μ moles/1 SDS			15 μ mole/1 DTAB		
Sample	Preparation	pH	Electrophoretic Mobility μ cm/volt sec	pH	SDS Adsorbed molecules/ 100 Å^2	Electrophoretic Mobility μ cm/volt sec	pH	DTAB Adsorbed molecules/ 100 Å^2	Electrophoretic Mobility μ cm/volt sec
Beckjord	unwashed	8.8	-1.3	6.8	0	-4.1	10.1	0	+8.0
Fly Ash	washed	7.2	-8.9					0.43	
Kansas	unwashed	9.2	-1.3	7.3	2.1	-4.2	10.0	17.3	+8.2
Incin. Ash	washed	7.6	-7.1					0.47	
Lake Tahoe	unwashed	11.0	-0.40	8.9	5.2	-5.9	10.7	3.0	+6.9
Incin. Ash	washed	9.8	-5.8					0.95	
Millcreek	unwashed	9.7	-1.2	9.0	2.0	-4.3	10.5	4.6	+7.2
Incin. Ash	washed	9.5	-5.4					1.0	
Graphon	---	6.5	-1.3	8.0	2.3	-3.0	11.0	3.8	+2.23

were equilibrated with surfactant. The indicated pH values were taken at the time of measurement. The electrophoretic mobility results of the ashes in water, column 3, shows that the washing procedure greatly increases the zeta potential. The primary cause for this behavior is based upon electrical double-layer theory which predicts that the double-layer thickness is inversely proportional to the square root of the ionic concentration. Since the zeta potential is actually the electrical potential at some distance from the surface, and since this potential decays somewhat exponentially as a function of distance from the surface, then the zeta potential would increase with decreasing ionic concentration even when the surface potential remains constant. A good measure of the ionic concentration is the conductivity which has been shown (see Figure 7) to decrease with increasing number of washings for all four ashes. Therefore, the observed increases in the electrophoretic mobility, and hence zeta potential, for the washed ashes can be due solely to the decrease in ionic concentration. Furthermore, the lower electrophoretic mobilities for washed Lake Tahoe and Millcreek (5.8 and 5.4 as compared to 7.1 and 8.9 for Kansas and Beckjord respectively) can be attributed to compression of the double layer as deduced from the higher conductivities observed for these two samples after twenty washings.

The electrophoretic mobility results of the unwashed ashes equilibrated with surfactant are given in columns 6 and 9 for the anionic SDS and cationic DTAB covered surfaces, respectively. Although the solution adsorption results on the unwashed ashes were not reliable, the electrophoretic mobility measurements are considered a true measure of the relative amounts of surfactant adsorbed on each surface. The anionic SDS produces a negative charge for all the ashes with Lake Tahoe yielding the highest value of 5.9 μ cm/volt sec. Likewise the cationic DTAB produces a positive charge for all the ashes with Lake Tahoe exhibiting the smallest electrophoretic mobility of 6.9 μ cm/volt sec. Although these results appear to be in conflict with the DTAB adsorption results on the washed ashes, where Lake Tahoe, along with Millcreek, adsorbs twice as much DTAB than the remaining ashes (see Figure 17), the washing procedure is capable of changing the surface properties with respect to its positive or negative character. The conclusion drawn from these results is that the unwashed Lake Tahoe surface relative to the other ash samples, has a more positive character. The washing procedure, furthermore, has the effect of rendering the surface more negative, and hence more susceptable to cationic adsorption.

The settleability experiments on activated sludge, i.e., measurements of the height of clear supernatant in a sedimentation tube as a function of time, were carried out over the entire two year period of this program. The dry solids concentration of this sludge was 0.2%. Figure 18 is a representative graph which shows the change in the rate of settling after adding 50 mg of ash to 25 ml of activated sludge, or an ash to dry sludge solids ratio, A/S, of one. The dotted line represents the settling of the activated sludge itself over the period of the run. All four ashes used had a marked effect on the rate of settling of activated sludge,

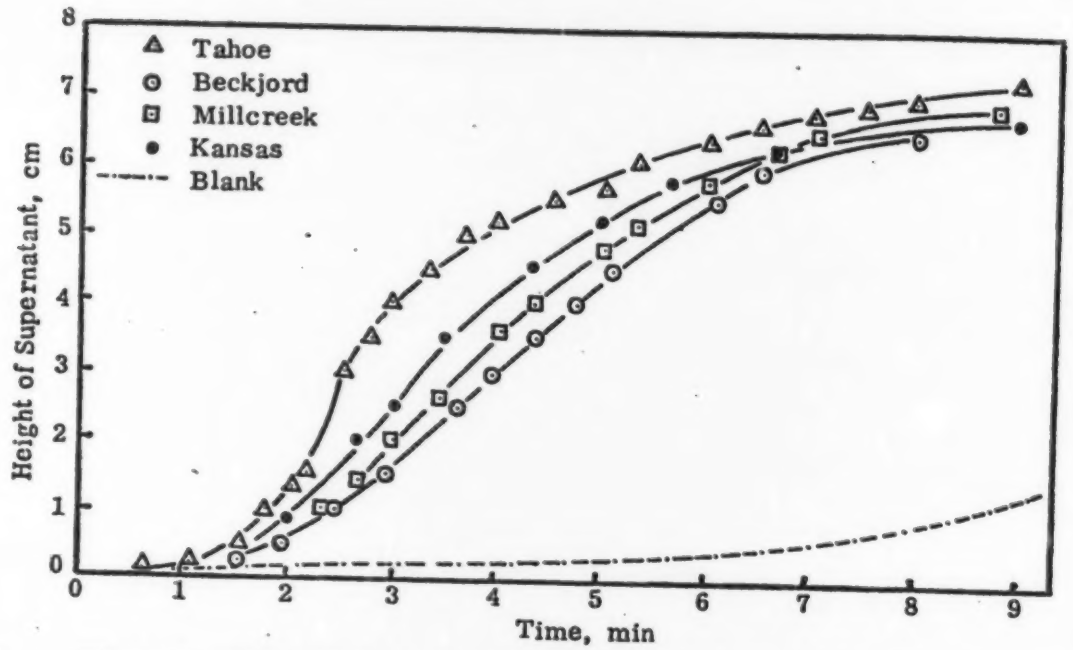

Figure 18 - Settleability of Activated Sludge for 50 mg. of Ash Additives, A/S = 1 (for 25 ml of sludge in 15 cm long test tube).

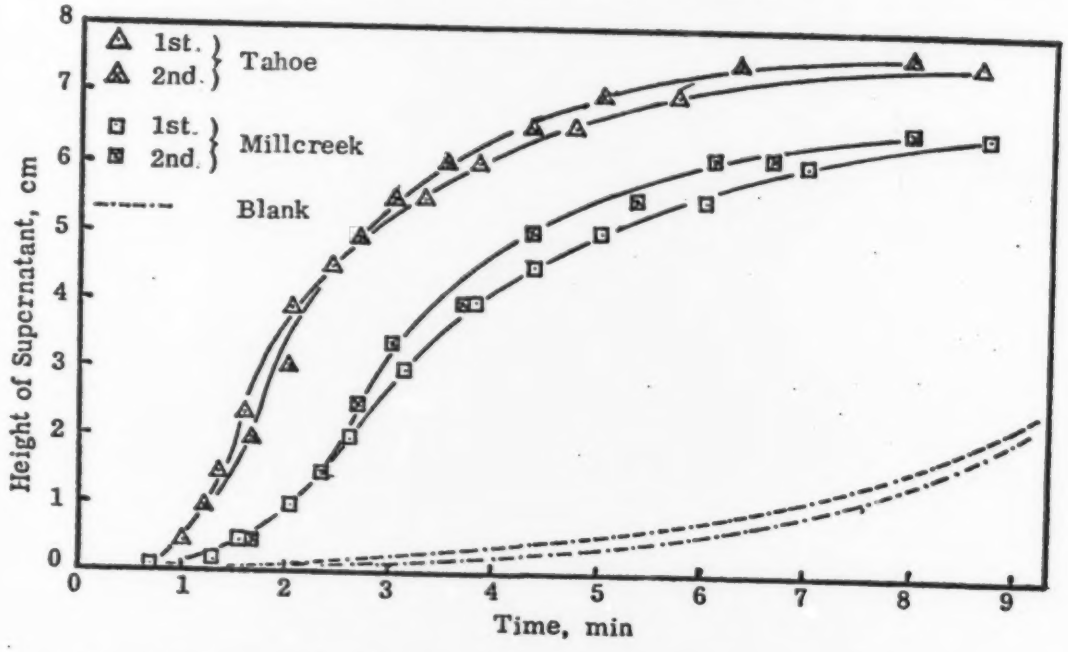

Figure 19 - Reproducibility in Settleability Efficiency of Tahoe and Millcreek Additives (25 ml of sludge in 15 cm long test tube).

though the efficiency in settleability of the different ashes always appeared to be in the order:

Tahoe > Kansas > Millcreek > Beckjord

An interpretation of settleability results must be influenced by the reproducibility of the experimental runs. A major effort was made to determine the source of experimental errors and their orders of magnitude. Figures 19 and 20 give typical results obtained when the measurements were carried out approximately 30 minutes apart on the same batch of activated sludge and by different operators. The small variation obtained in the settleability rate was found to be due primarily to the aging time of the sludge, which agrees with sludge aging results of previous authors. Longer periods of aging, i. e. more than an hour without aeration, has resulted in pronounced deviations as the sludge deteriorates with time. Figure 21 gives the variation in settleability for 50 mg of Lake Tahoe ash added to activated sludge samples which were obtained over a 12 month period. Line "a" represents the maximum measured efficiency, line "b" the minimum, and the dotted line the average of 18 determinations. The shaded area indicates the variation in settleability of the sludge alone. Similar curves were obtained for the other ashes added to activated sludge. In general, measurements which fell well below the average were readily predictable from the properties of the sludge alone and usually occurred after extensive rainfalls or during vacation periods when the percent of solids was low.

The settleability as a function of additive concentration was investigated for all four ashes. Typical results are given in Figures 22, 23, 24 and 25 for Lake Tahoe, Kansas, Millcreek and Beckjord, respectively. The three concentrations of additive were: 10 mg, 50 mg and 100 mg per 25 ml of sludge or A/S of 0.2, 1.0 and 2.0 respectively. The results showed that the settling rate was a very sensitive function of the additive concentration for all four ashes. The effect of higher concentrations of additives were also measured, but the settling rate was too rapid to give reproducible or reliable results by this experimental technique. Other investigators have found increased improvements in sludge filterability with increasing concentration of ash.

Previous results in this report have shown that all four ashes contain an appreciable amount of water soluble salts as demonstrated by the fact that they all increase the conductivity and pH of distilled water. In order to determine the mechanism which brings about increased settling rate of activated sludge, a comparison was made of the rate of settling activated sludge after adding unwashed ash, ash which had been washed at least 10 times with distilled water and ash washings, i. e. the water soluble salts which were obtained from 50 mg of ash in 25 ml of distilled water. Figures 26 through 29 give representative graphs of the results obtained in the comparison experiments when 50 mg of solid additive was added to the sludge. The results, which were similar for other concentrations, showed that all three

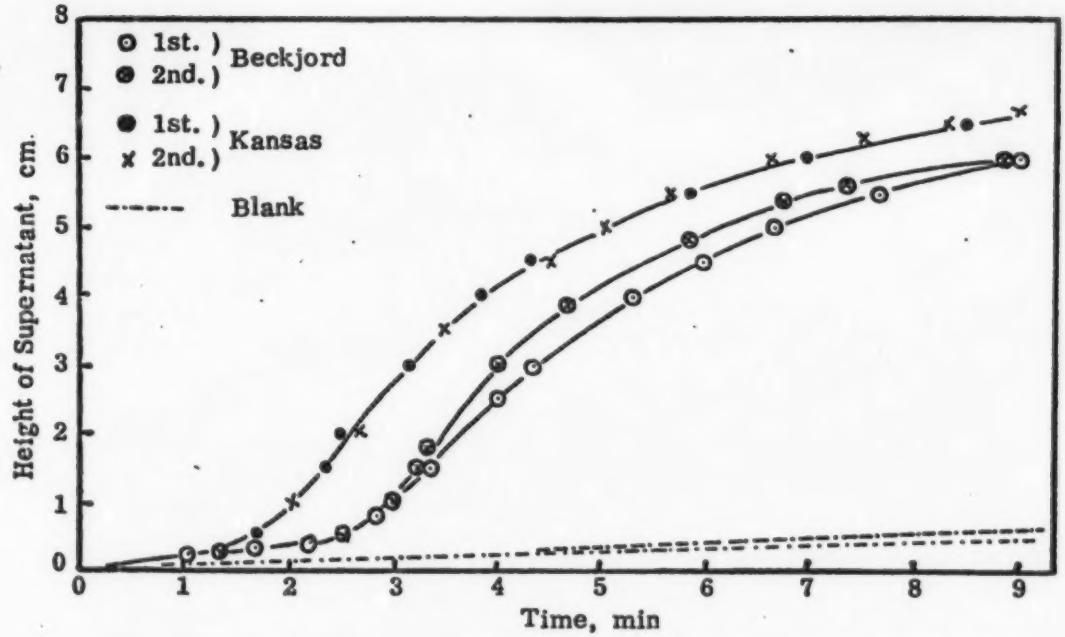

Figure 20 – Reproducibility in Settleability Efficiency of Beckjord and Kansas Additives (25 ml of sludge in 15 cm long test tube).

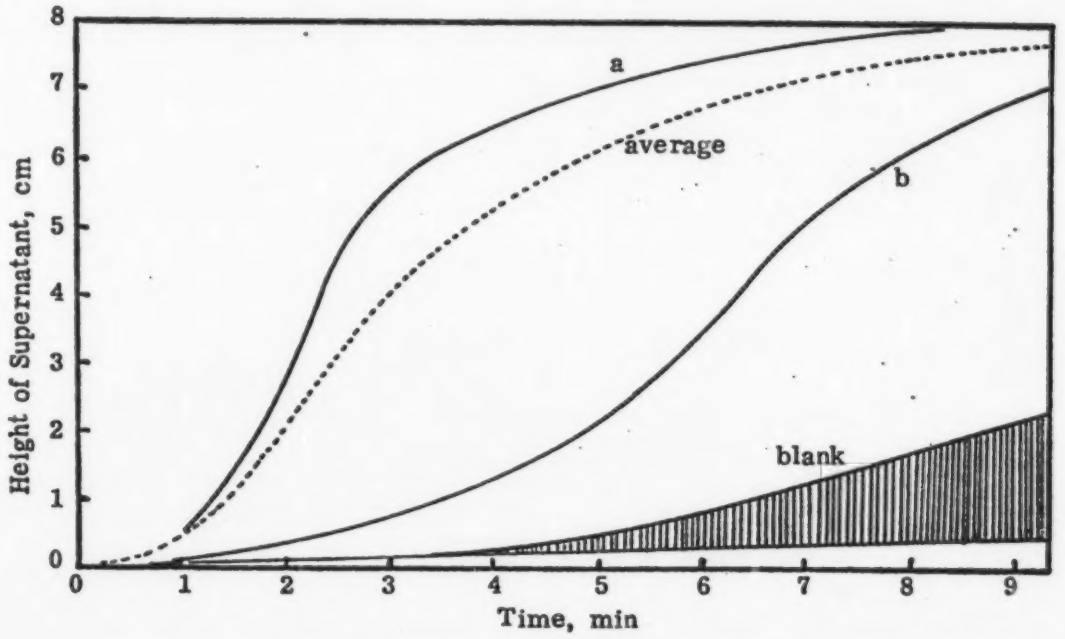

Figure 21 – Reproducibility in Settleability Efficiency of Tahoe Ash Over a 12-Month Period (25 ml of sludge in 15 cm long test tube).

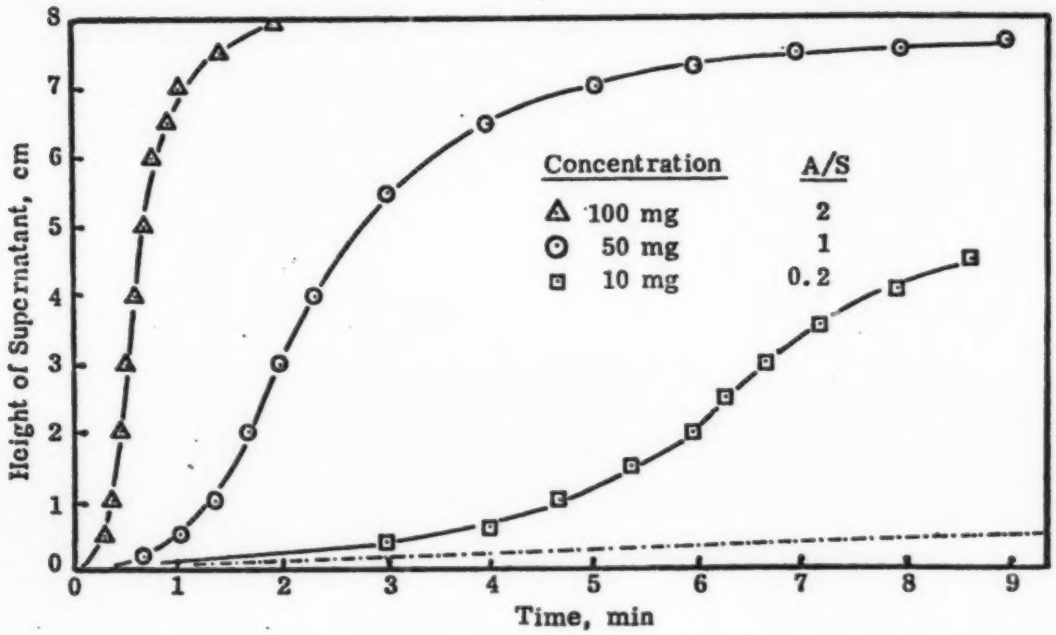

Figure 22 – Settleability of Activated Sludge as a Function of Concentration of Lake Tahoe Additive (25 ml of sludge in 15 cm long test tube).

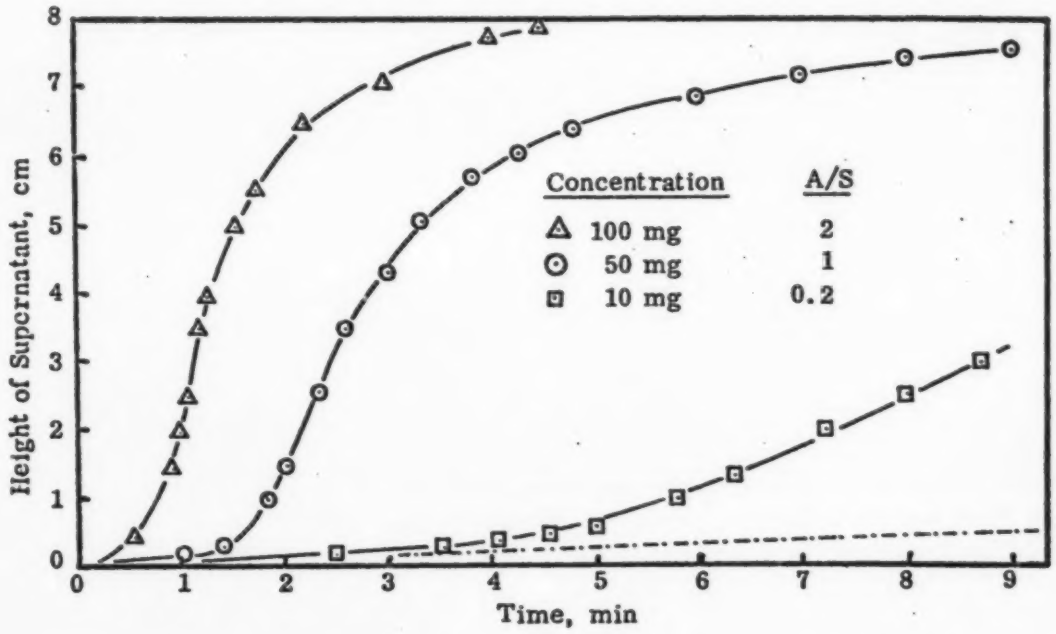

Figure 23 – Settleability of Activated Sludge as a Function of Concentration of Kansas Additive (25 ml of sludge in 15 cm long test tube).

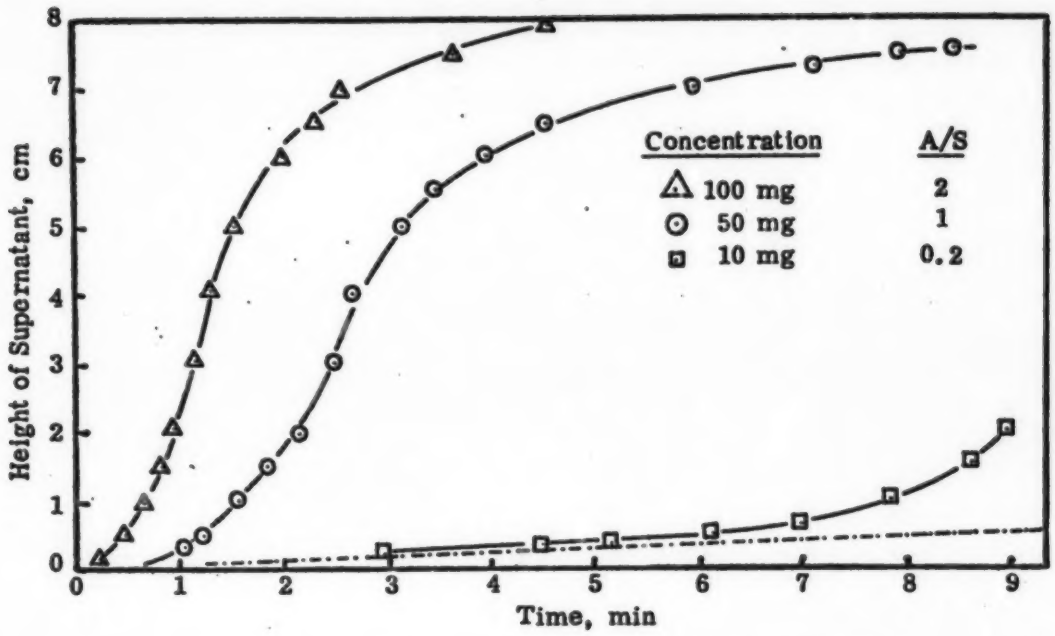

Figure 24 – Settleability of Activated Sludge as a Function of Concentration of Millcreek Additive (25 ml of sludge in 15 cm long test tube).

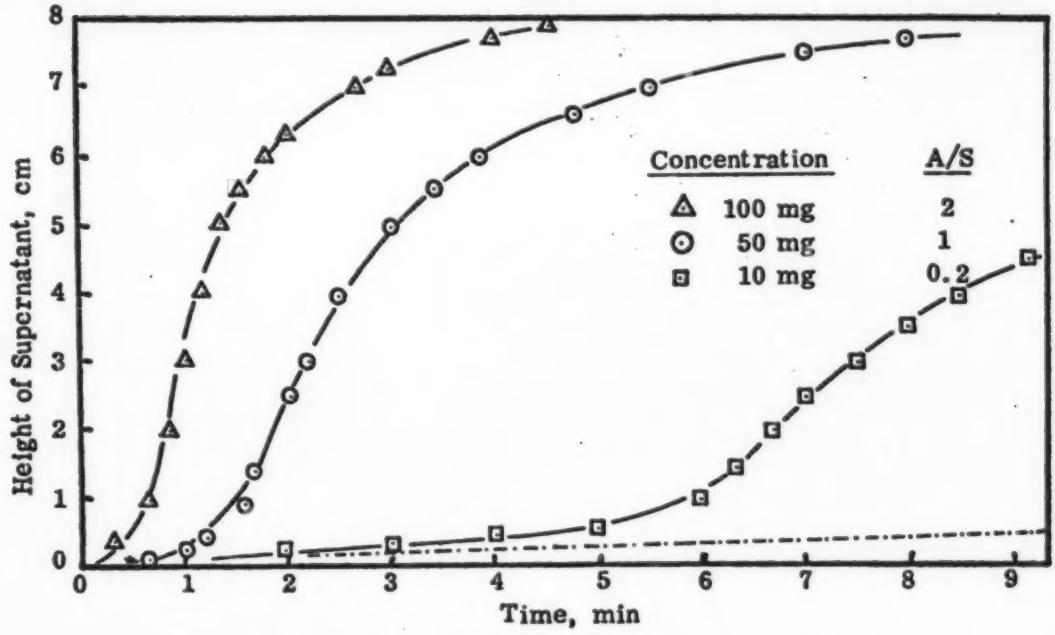

Figure 25 – Settleability of Activated Sludge as a Function of Concentration of Beckjord Additive (25 ml of sludge in 15 cm long test tube).

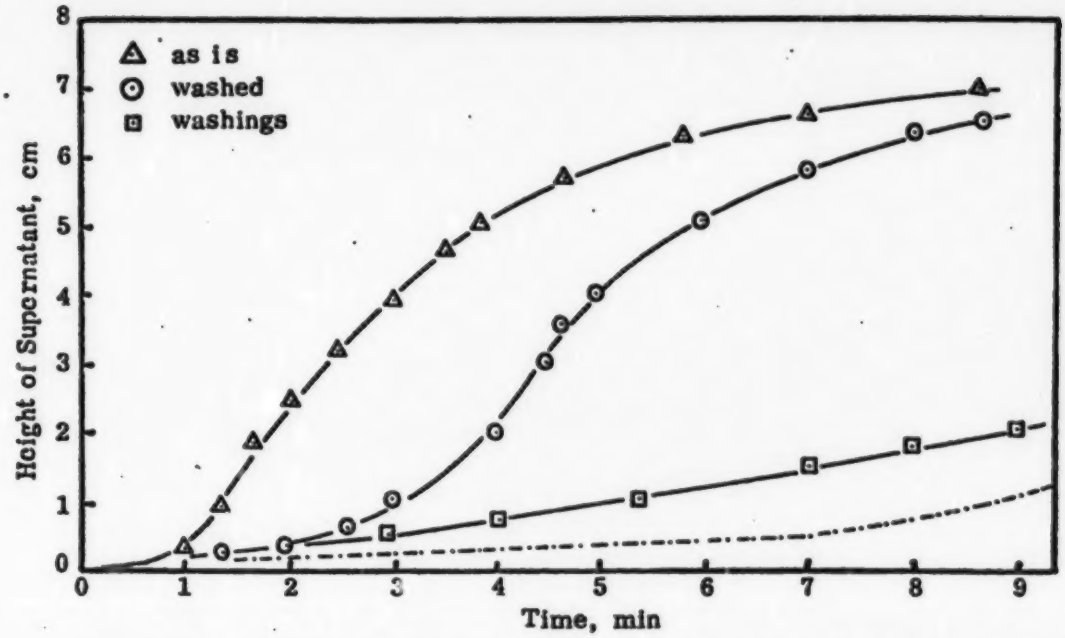

Figure 26 – Comparison of Washed Ash, Unwashed Ash, and Ash Washings for Lake Tahoe Additives on Settleability (25 ml of sludge in 15 cm long test tube).

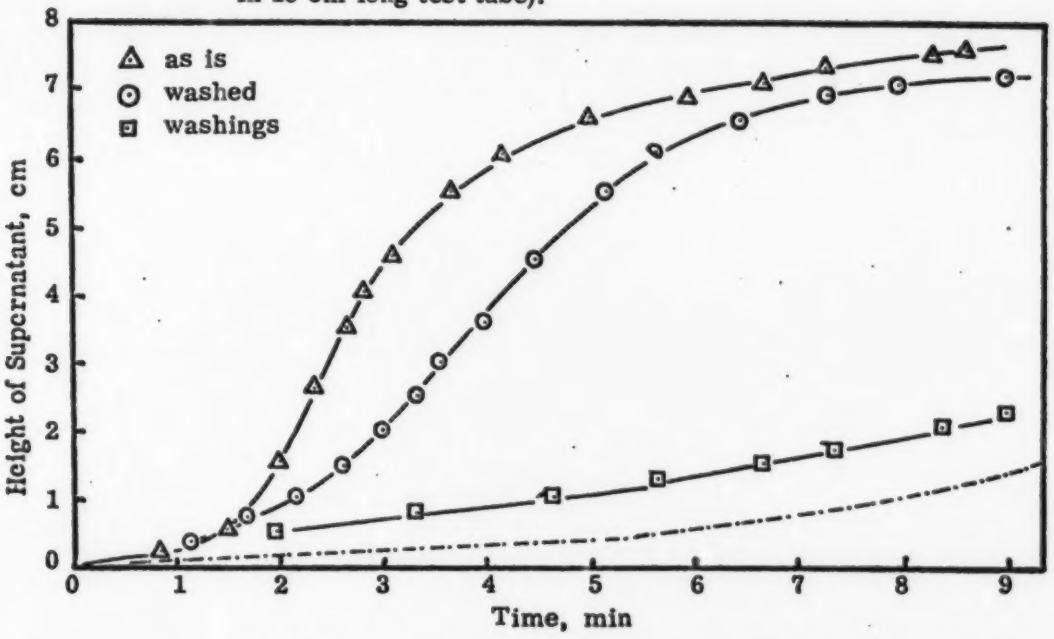

Figure 27 – Comparison of Unwashed (Total) Ash, Washed Ash and Ash Washings for Kansas Additives on Settleability (25 ml of sludge in 15 cm long test tube).

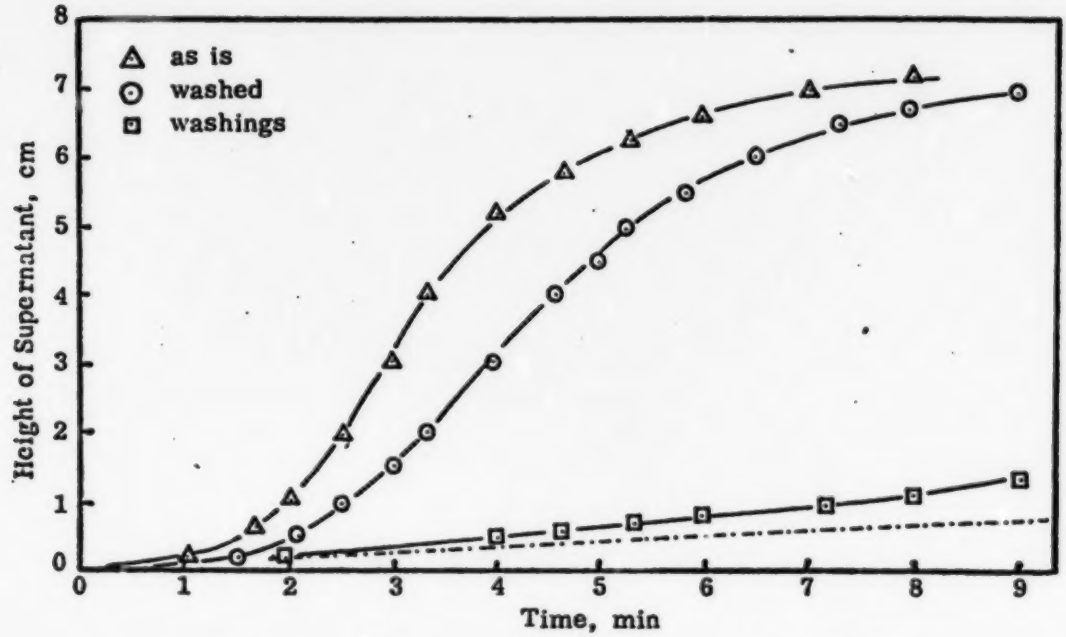

Figure 28 – Comparison of Unwashed Ash, Washed Ash and Ash Washings for Millcreek Additive on Settleability (25 ml of sludge in 15 cm long test tube).

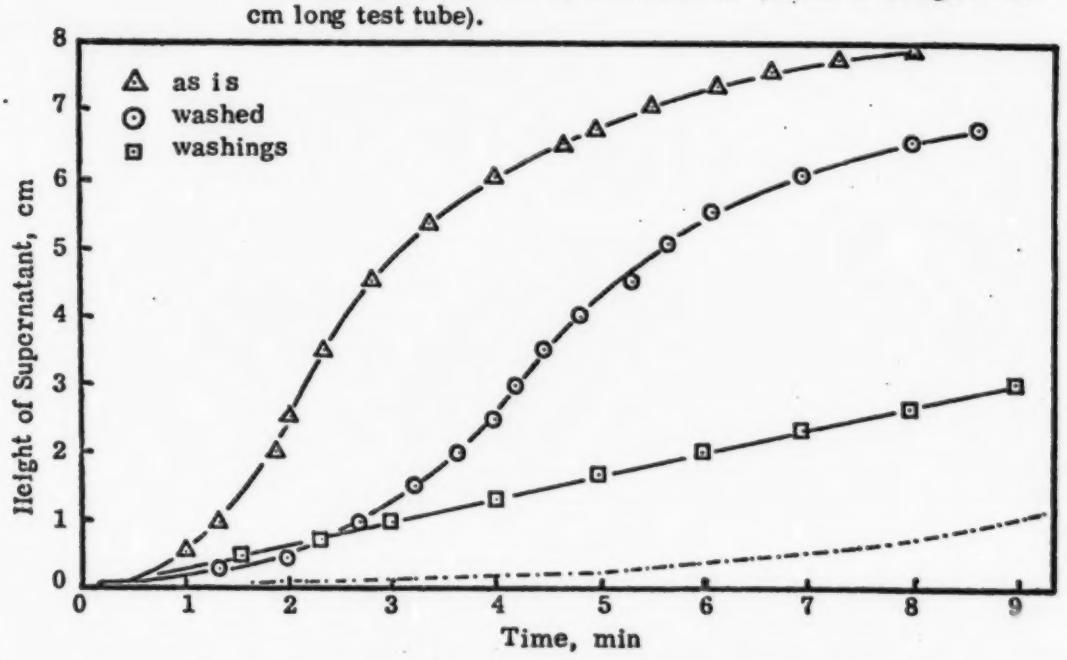

Figure 29 – Comparison of Unwashed Ash, Washed Ash, and Ash Washings for Beckjord Additive on Settleability (25 ml of sludge in 15 cm long test tube).

samples of each ash, i. e. unwashed ash, washed ash and washings, improved the settling rate, though the efficiency was found to be:

unwashed ash > washed ash > ash washings

The washings obtained from Kansas, Lake Tahoe and Millcreek incinerator ashes effected only a small increase in the settling rate, while the washing obtained from Beckjord fly ash showed a somewhat higher degree of efficiency. The washed ash samples showed the following order of efficiency:

Kansas > Millcreek > Beckjord > Tahoe

The most striking feature of these results was the reversal of Tahoe from the most efficient additive before washing to the least efficient after washing. The implication of these results is that more than one mechanism is important for inducing flocculation of sludge particles. Apparently the surfaces of the additives act as adsorption centers while the water soluble materials complex with other molecules or adsorb onto the surface of the sludge particles. The solid/liquid interfacial properties of the sludge particle can thus be altered so as to induce flocculation.

The different size fractions of Beckjord fly ash were investigated because of their unusual properties. The large size fraction, i. e. 725 microns, was black in color and about 75% of this fraction was found to be magnetic in character, probably due to the presence of magnetite as identified by X-ray analysis. The smaller size fraction, < 38 microns, on the other hand, was gray-brown in color with less than 30% of the particles exhibiting magnetic properties. Figures 30 and 31 show the effects of the large and small particle size fractions of Beckjord, for two different concentrations, on the settleability rate. In both cases the order of efficiency was:

total ash > small particle size > large particle size

These results cannot be explained based on the specific surface area information, Table 1, where the large particle size had an area three times greater than the total ash and nine times greater than the small particle size fraction. It appears that the composition differences of the two fractions were of primary importance in these results.

Four samples, whose surface properties have been well characterized, were investigated for their effect on settleability. The four samples were: Quso H-40, a precipitated silica whose surface was 100% hydrophilic; Cab-o-sil M-5, a fumed silica whose surface was 20% hydrophilic; graphon, a 100% hydrophobic homogeneous surface; and carbon black Elf-4, whose surface was amorphous and contained from 5% to 10% polar sites. All of these samples were considered pure in the sense

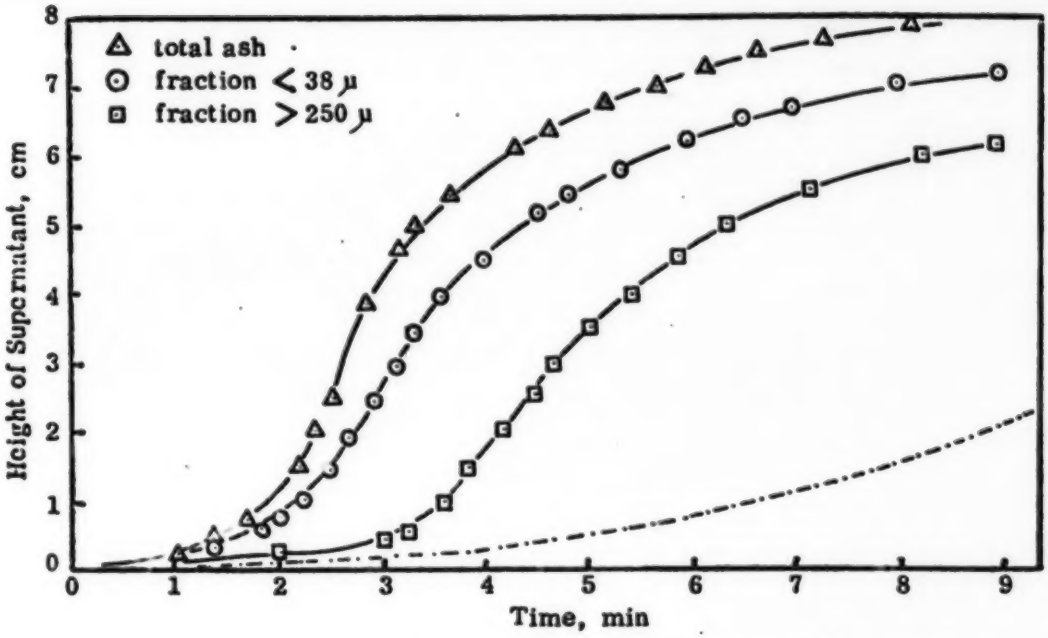

Figure 30 – Effect of Different Particle Size Fraction of 50 mg of Beckjord Additive on Settleability (25 ml of sludge in 15 cm long test tube).

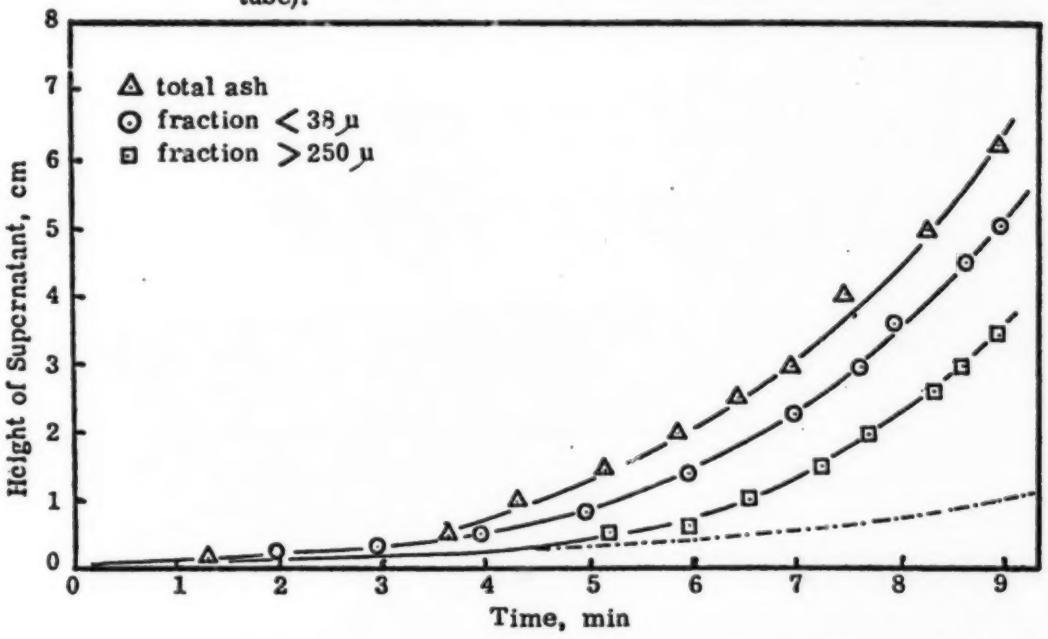

Figure 31 – Effect of Different Particle Size Fractions of 10 mg of Beckjord Additive on Settleability (25 ml of sludge in 15 cm long test tube).

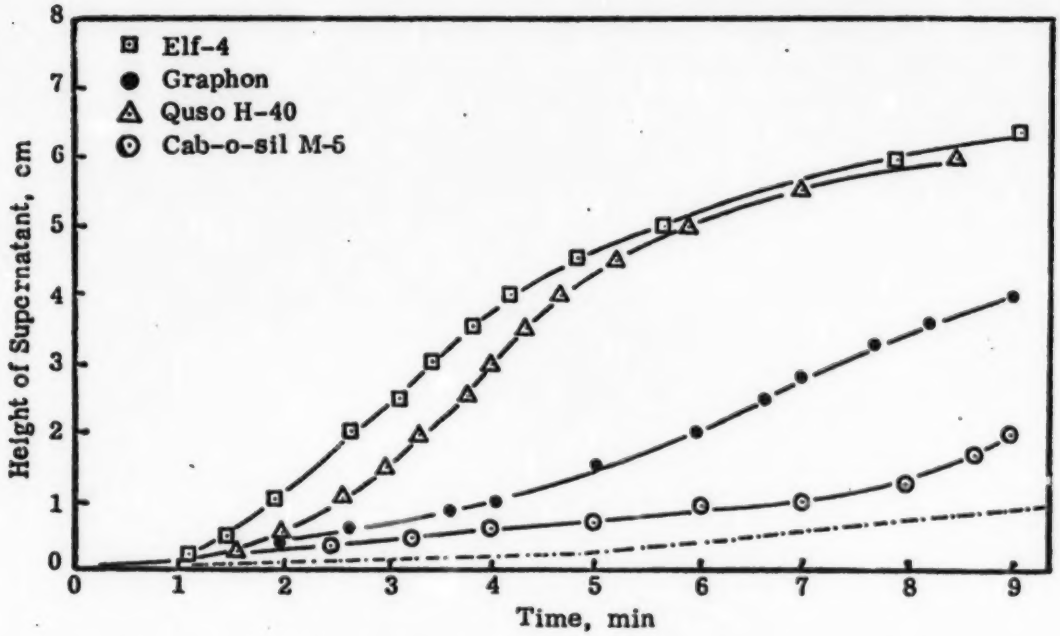

Figure 32 - Comparison between the rates of Settleability for 50 mg Carbon and Silica Additives, A/S of one (25 ml of sludge in 15 cm long test tube).

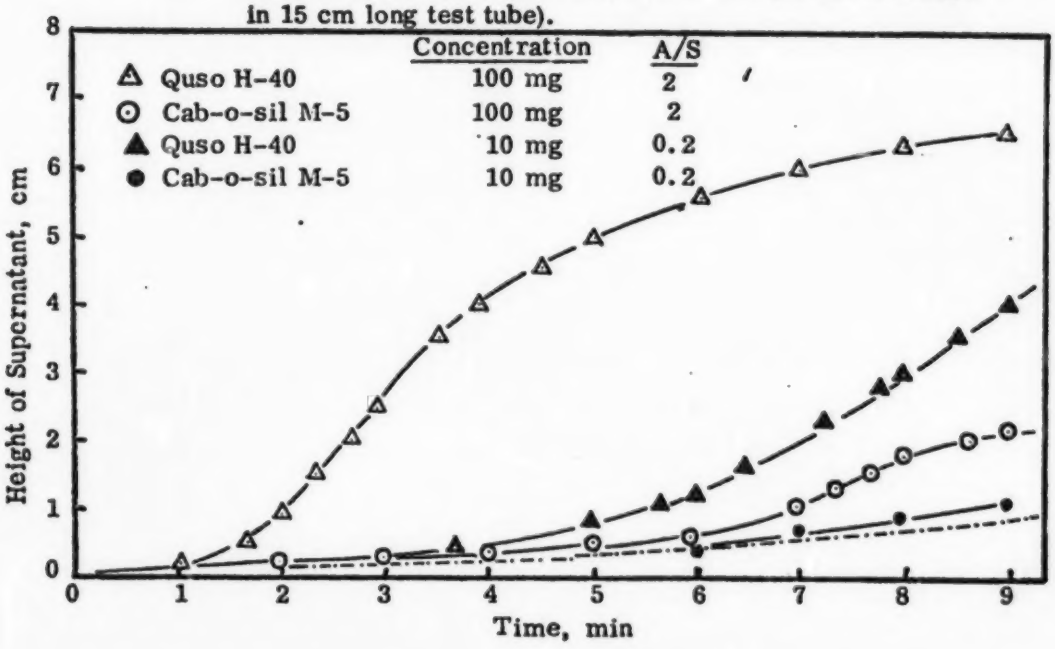

Figure 33 - Settleability of Activated Sludge as a Function of Concentration for Two Silica Additives (25 ml of sludge in 15 cm long test tube).

that they contained no water soluble materials. The results for all four samples at concentrations of 50 mg of additive per 25 ml of sludge, are presented in Figure 32. Both Elf-4 and Quso H-40 were greatly superior to graphon and Cab-o-sil M-5 for increasing the settleability. Figures 33 and 34, which compare the samples at different concentrations, confirm the above findings. Since all four samples exhibit about the same surface area (graphon 80 m^2/g, Elf-4 110 m^2/g, Quso H-40 133 m^2/g, and Cab-o-sil M-5 180 m^2/g), and contain no water soluble salts, the difference in settleability efficiency must be attributed to the surface properties. The mechanism operating on these systems, therefore, must be primarily attributed to adsorption on the surface of the additives followed by a change in the solid/liquid interfacial properties of the solids present in the sludge which ultimately lead to flocculation. The solution adsorption results of DTAB at neutral pH, Figures 14 and 15, support the proposed mechanism in that they show significantly higher adsorption capacity for Quso H-40 and carbon black Elf-4 as compared to Cab-o-sil M-5 and graphon.

A sample of magnetite was utilized as an additive at the three concentrations of 10 mg, 50 mg and 100 mg per 25 ml of sludge, Figure 35, because of the presence of large concentrations of this material in Beckjord fly ash. The results show that this material was very effective for increasing the settleability, and even more effective than Beckjord fly ash. Since no water soluble salts were present on the magnetite surface, these results support the mechanism proposed above whereby solution adsorption of a surface can lead eventually to flocculation. Unfortunately not enough was known about the surface properties of either the magnetite or the activated sludge to be specific about the nature of these interactions.

A number of water soluble salts and polymeric flocculants were used as additive for activated sludge in order to investigate the possibility of flocculation occurring by mechanisms other than the ones already proposed. Two halides, calcium fluoride and aluminum chloride, Figures 36 and 37, were found to be very effective for inducing flocculation. The effect of potassium phosphate, Figure 37, was also measured and found to have very little effect. The effects on the settleability of activated sludge were measured for a number of commercial grade polymeric flocculants, Figures 38 and 39. 10 ml of flocculant/25 ml of sludge, or a flocculant to dry solids ratio of 0.2, was added in each experiment. Figure 38 gives the results of the Atlas flocculants of different ionic character as specified by the manufacturer. The most effective additive was cationic while the least effective was nonionic. Figure 39 gives the results of the anionic Nalco surfactant which yielded a small but measurable increase in the settling rate. The fact that the cationic surfactant was more effective was not surprising since the activated sludge was slightly alkaline and these solid surfaces were expected to be negative in character. A more precise interpretation of these results was not possible because of the limited information available about the nature of the flocculants.

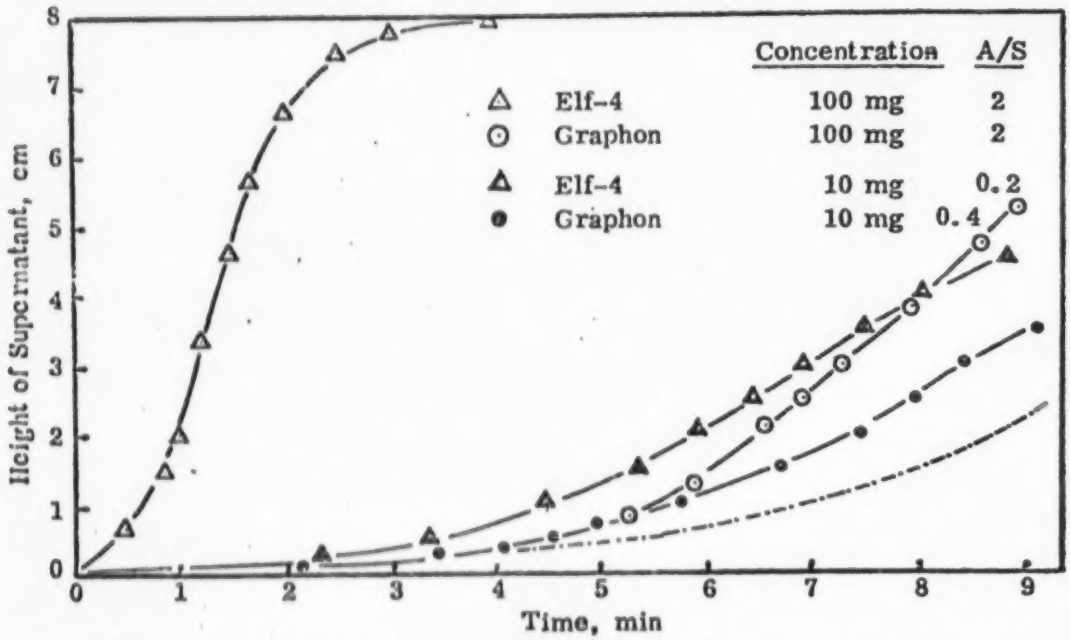

Figure 34 - Settleability of Activated Sludge as a Function of Concentration of Carbon Additives (25 ml of sludge in 15 cm long test tube).

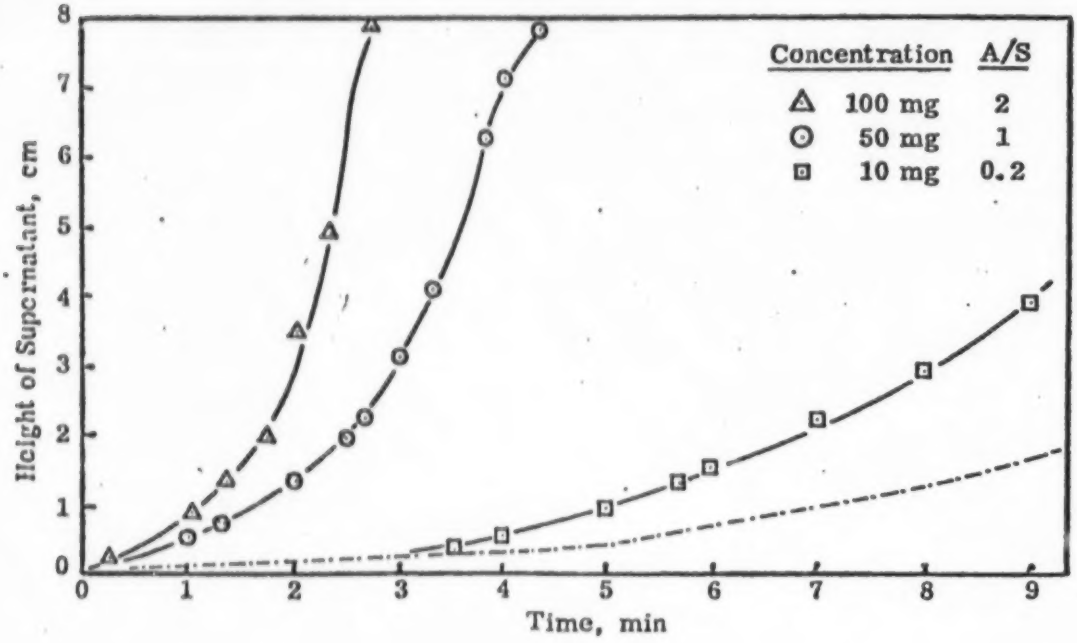

Figure 35 - Settleability of Activated Sludge as a Function of Concentration of Magnetite Additive (25 ml of sludge in 15 cm long test tube).

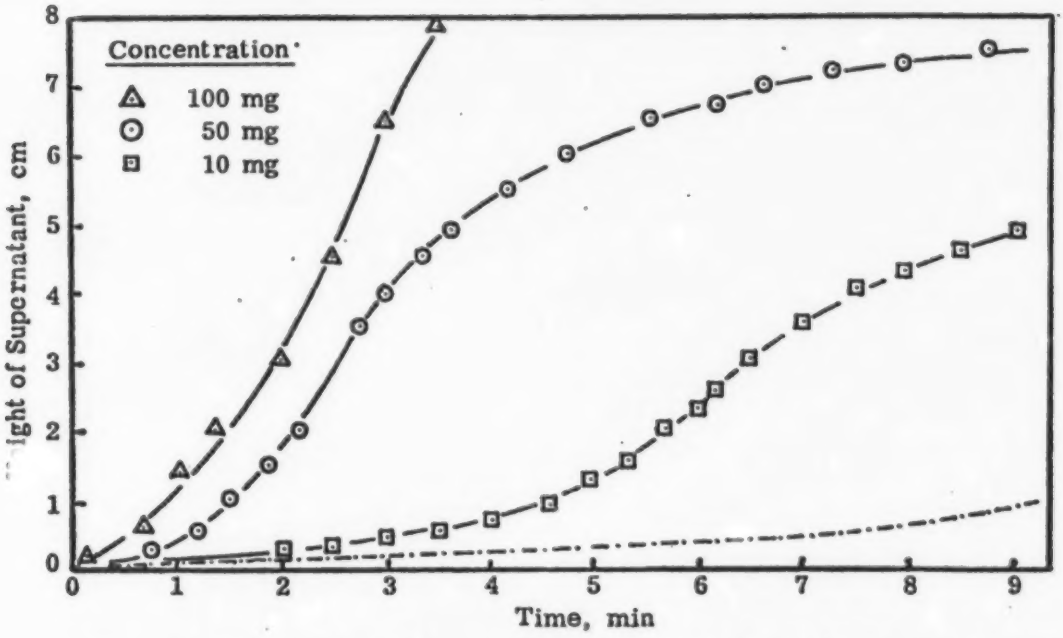

Figure 36 – Settleability of Activated Sludge as a Function of Concentration of Calcium Flouride Additive (25 ml of sludge in 15 cm long test tube).

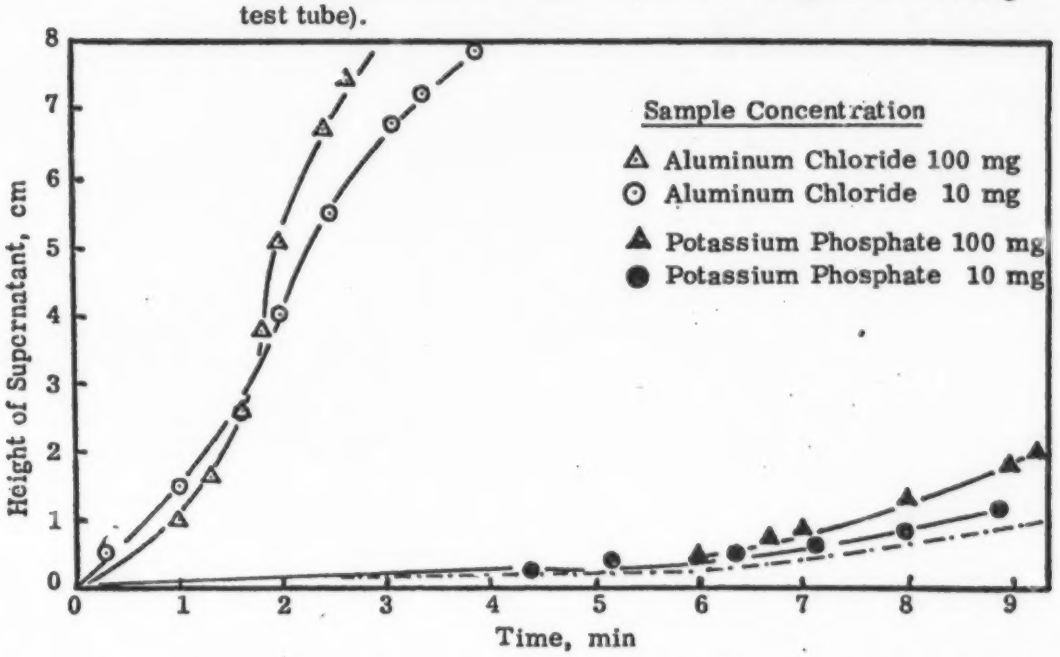

Figure 37 – Settleability of Activated Sludge as a Function of Concentration of Aluminum Chloride and Potassium Phosphate Additives (25 ml of sludge in 15 cm long test tube).

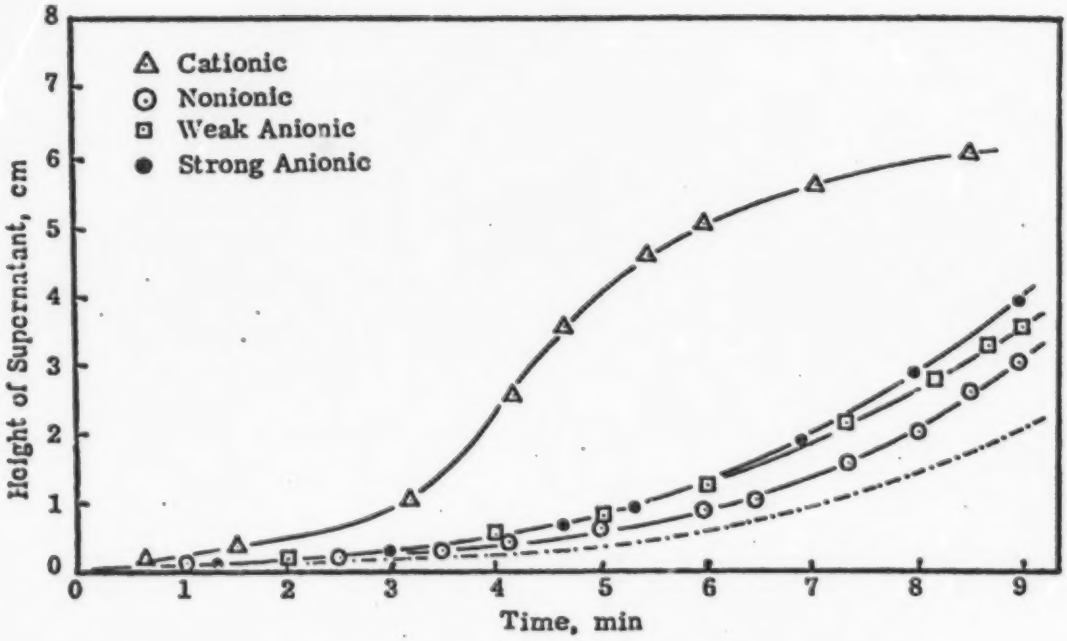

Figure 38 – Settleability of Activated Sludge for Different Atlas Polymeric Flocculants (10 mg of flocculant per 25 ml of sludge in 15 cm long test tube).

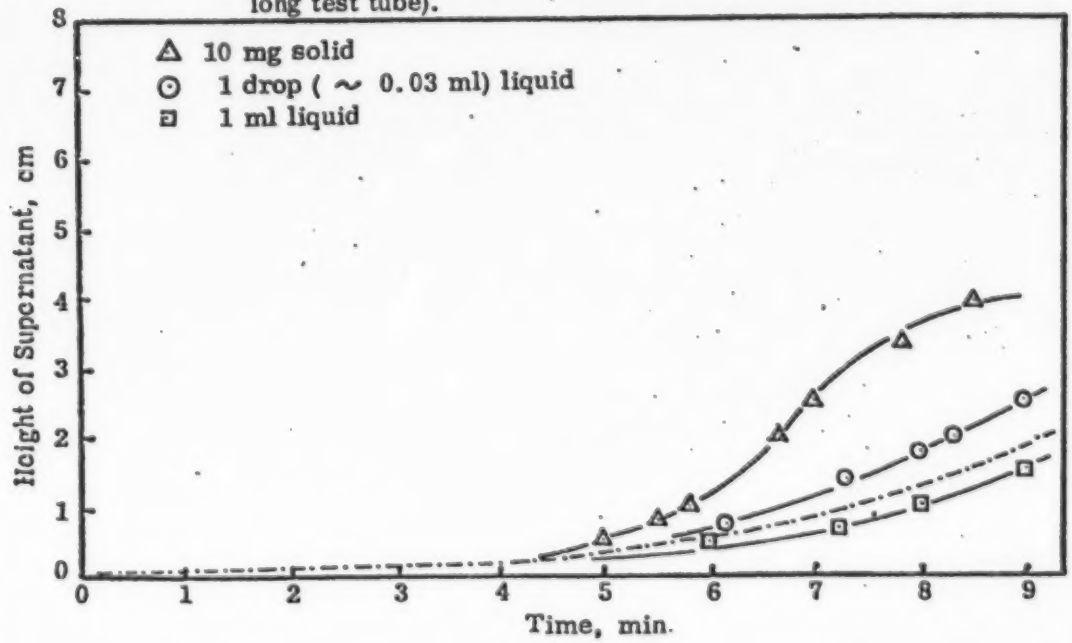

Figure 39 – Settleability of Activated Sludge for a Nalco Anionic Polymeric Flocculant (25 ml of sludge in 15 cm long test tube).

SECTION VI

DISCUSSION OF RESULTS

The surface properties and composition of the ash samples were characterized by a variety of experimental techniques. The pertinent features of this characterization may be summarized as follows:

1) The specific surface areas of the ash samples ranged from 1.6 m^2/g, for Beckjord fly ash, to 17 m^2/g for Lake Tahoe incinerator ash. This information, along with the particle size distribution, indicates that all ashes are porous with the Lake Tahoe ash exhibiting a higher degree of porosity.

2) The X-ray diffraction results show that quartz is present in all four ash samples. Magnetite is present in both the Lake Tahoe and Beckjord ashes. Fluor-apatite and/or Lewistonite, which contains sodium, potassium, phosphate, fluoride and calcium ions, was detected only in Lake Tahoe sample.

3) All four samples contain a significant concentration of water soluble salts which are predominately alkaline with Lake Tahoe and Millcreek ashes containing enormous concentrations which could not be removed by multiple washings.

4) The water and isopropanol gas adsorption isotherm results indicate a high degree of hydrophilicity for the surfaces of all four ash samples. The results also show that the ashes exhibit properties which are more characteristic of a silica surface than a carbon surface.

5) The solution adsorption results show that the ash samples are capable of adsorbing up to one molecule/100 $Å^2$ of cationic surfactant DTAB, dodecyltrimethylammonium. Since the theoretical maximum level of adsorption for this molecule is 3.5 molecules/100 $Å^2$, approximately 30% of the ash surface is active with the remaining surface probably being excluded due to pores.

6) Electrophoretic mobility measurements indicate that all four ashes exhibit a relatively strong negative charge in water.

The relative efficiency of the ashes in assisting the dewatering of activated sludge was evaluated by settleability experiments. The advantages and disadvantages of this experimental technique must be exposed before evaluating the results. The rate of settling of a dilute suspension is directly proportional to the degree of particle-particle interaction. When the suspension becomes more concentrated, especially when the solid particles have irregular shapes, the rate of settling would be expected to first increase and then decrease with increasing particle-particle interaction as structure is formed in the suspension. A further increase in particle-particle interaction can potentially, but not necessarily, result in a breakdown of this structure with a resulting increase in the settling rate. An analogous situation exists in measuring rate of filtering where intermediate flocculation results in a high degree of structure and, hence, a porous filter cake. The main advantages of working with a dilute system is that the settling rate is a sensitive function of the degree of flocculation and always increases with increasing flocculation. The disadvantage is that the rate of settling cannot be followed for long periods of time because the clear supernatant interface becomes obscure for relatively stable suspensions.

The settleability results showed that all four ashes had a pronounced effect on the rate of settling of activated sludge, which is in agreement with Tenney and Echelberger [4], and investigators at the Taft Center, Cincinnati, Ohio, with the efficiency being in the order of

Tahoe > Kansas > Millcreek > Beckjord

When the ashes were extensively washed the order of efficiency was

Kansas > Millcreek > Beckjord > Tahoe

The only important change here was that the Tahoe ash went from the most efficient additive to the least efficient after washing. The unwashed ashes, furthermore, were always more efficient than the washed ashes which were more efficient than the ash washings. A number of halide salts and cationic polymeric flocculants were found to appreciably increase the rate of settling activated sludge. Certain pure solids, i.e. hydrophilic silica, carbon black and magnetite, greatly increased the settling rate while hydrophobic silica and graphon had very little effect on the settling rate.

There are two possible mechanisms which are capable of inducing flocculation of sludge solids: 1) reduction of inter-particle coulombic repulsion by either compression of the electrical double-layer through increased electrolyte concentration, or by reduction of the surface charge density through counterion adsorp-

tion or desorption of potential determining ion, and 2) introduction of solid additives which interact with sludge particles and, hence, would be capable of acting as a bridge between sludge particles. The fact that the anionic polymeric surfactants had no effect while the cationic surfactant appreciably increased the settling rate strongly suggests the negative charge on the sludge particle surface is reduced by ionic adsorption which leads to flocculation. The introduction of halide salts also leads to a reduction in coulombic repulsion either by adsorption of cations, or compression of the electrical double-layer. The fact that hydrophilic silica, carbon black and magnetite had an even greater effect in increasing the settling rate leads to the conclusion that these surfaces strongly interact with sludge solids and bring about flocculation by bridging particles together. Since hydrophobic silica and graphon had essentially no effect on the settling rate, the surface properties of the solid additives, especially with respect to ionic adsorption, must be an important parameter for inducing flocculation.

The four ash additives, which contain solid particles and a high concentration of water soluble salts, are capable of inducing flocculation of sludge solids according to all the mechanisms proposed above. The fact that extensive washing of all four ashes had the effect of reducing, but not eliminating, their efficiency for increasing the settling rate supports the hypothesis that both the ionic salts and solid particles play an important, and possible independent, role in the sludge conditioning process. A direct correlation between the surface properties of the ash additives and the efficiency of increased sludge settleability, however, cannot be made in any meaningful manner. For example, the Lake Tahoe ash is reduced from the most efficient to the least efficient additive after extensive washing. While the initial high efficiency may be attributed to the initial high concentration of water soluble salts present on the Lake Tahoe ash surface, the reduction in relative efficiency after washing is difficult to explain since the Lake Tahoe ash still retains the highest concentration of water soluble salts under these conditions. There is very little difference, furthermore, in the surface properties of the Lake Tahoe ash before and after washing as compared with the other ash additives. An extension of this work should include an investigation of the solid/liquid interfacial properties of the various ashes in the supernatant of the activated sludge.

The settleability results of the carbon black, silica, and surfactant additives, however, are rather definitive. These results, along with the settleability results for the ash additives do lend themselves towards the postulation of some definite mechanisms for increasing the settling rate of activated sludge. The hydrophilic carbon and silica additives are generally intermediate in settleability efficiency between the unwashed and washed additives. The fact that only cationic surfactant additives increase the settling rate of activated sludge indicates that the sludge solids have a negative charge which is neutralized by surfactant adsorption. These results lead to the following conclusions concerning the mechanism of increased settling rate of activated sludge due to solid additives:

1. the solid additives interact strongly with the negatively charged sludge solids so as to induce flocculation by bridging. A high concentration of polar sites is necessary to reduce or change the negative charge on the solid additive surface.

2. the presence of water soluble salts, which are present on the ashes, or cationic surfactants have the effect of reducing the negative charge present on the surface of the sludge solids so that the sludge solids may interact directly in the absence of coulombic repulsion.

SECTION VII

REFERENCES

1. Vater, W., "European Practices in Sludge Digestion and Disposal," in Water Quality Improvement by Physical and Chemical Processes, Water Resources Symposium No. 3, by E. F. Gloyna and W. W. Eckenfelder, Jr., University of Texas Press, Austin, 1970, pp. 421-436.

2. Tenney, M. W. and Cole, T. G., "The Use of Fly Ash in Conditioning Biological Sludges for Vacuum Filtration," Journal Water Pollution Control Federation, 40, R281-R302 (1968).

3. Eye, J. D. and Basu, T. K., "The Use of Fly Ash in Wastewater Treatment and Sludge Conditioning," Journal Water Pollution Control Federation, 42, R125 (1970).

4. Tenney, M. W. and Echelberger, W. F., "Fly Ash Utilization in the Treatment of Polluted Waters," presented at the Second Ash Utilization Symposium, Pittsburgh, Pa., March 10-11, 1970.

5. Smith, J. E., Hathaway, S. W., Farrell, J. B. and Dean, R. B., "Sludge Conditioning with Incinerator Ash," presented at the 27th Purdue Industrial Waste Conference, May 2-4, 1972.

6. Adamson, A. W., "Physical Chemistry of Interfaces," Interscience Publishers, New York, Chap. XIII, (1967).

7. Walker, Philip L., "Chemistry and Physics of Carbon," Vol. 6, 191 (1970).

8. Parker, Randall and King, Journal Water Pollution Control Federation, (1972).

9. Barr, T., Oliver, J. and Stubbings, W. V., Journal of the Society of the Chemical Industry, 67, 45 (1948).